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THE

PHYSICAL REVIEW.

CHANGE OF PHASE UNDER PRESSURE.

II. NEW MELTING CURVES WITH A GENERAL THERMODYNAMIC DISCUSSION OF MELTING.

BY P. W. BRIDGMAN.

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Introduction.
Detailed Data for Nine Substances.
Thermodynamic Equation of the Melting Curve.*
Difference of Compressibility, Expansion, and Specific Heat between Liquid and Solid.
The Hypothesis of Schames.
The Effect of Chemical Constitution.
Summary.

INTRODUCTION.

IN the first paper of this series[1] data were given for the melting under pressure of eleven substances, four of which were found to have new polymorphic forms. The problems offered by polymorphic forms are of great interest and importance; since the writing of the first paper a number of substances have been investigated in this regard, and a number of new forms have been found. This question of polymorphism will be treated in future papers of this series. In the search for new forms a number of substances were investigated without result, whose melting curves lay within the temperature range of this work (0°–200°). These new melting curves are presented in this paper. Complete data are given for nine more substances, and fragmentary data for a few others. In addition, the melting curves of two other substances have been determined, but as these have more than one solid form, the data for them will be reserved for a future paper.

The discussion of melting given in the first paper was almost entirely concerned with the general character of the curve; as to whether it ends in a critical point, passes through a maximum temperature, or continues rising indefinitely. The data of the first paper seemed to point conclusively to only one conclusion, namely that within the range of at present realizable pressures there is nothing to indicate that the curve does not rise indefinitely. The data of this paper also all point to the same conclusion; the decreasing curvature of the melting curve and the convexity of the ΔV curve toward the pressure axis are shown by these substances also. The other two new substances with polymorphic forms show the same thing. Fig. 24, at the end of the paper, shows in a striking way that the shape of the melting curve is such that there cannot be a maximum temperature, as Tammann has supposed. In this diagram the slope of the melting curve is plotted against temperature. If there were a maximum, the curves would cross the temperature axis vertically. The direction of curvature shows that this cannot be the case at any temperature, no matter how high, unless there is a reversal of direction of curvature beyond the range of pressures at present realizable. If there is a maximum, these curves should be concave, instead of convex, toward the temperature axis. Up to the present, therefore, we have data on twenty two liquids, to four times the pressure range of previous measurements, all indicating the same answer to the question in hand, without exception. I shall, therefore, in future discussion consider this question as settled. It does not seem worth while to gather any more experimental evidence with this point only in view.

---

[1] P. W. Bridgman, PHYS. REV., N. S., Vol. 3, 126–203, 1914.

* Article to be concluded in next issue.

Besides the question as to the ultimate course of the melting curve, other questions are presented by the phenomena of melting. One question of interest is how the course of the melting curve is determined by the separate thermodynamic properties of solid and liquid. As is well known, this problem may be readily solved by the use of the thermodynamic potential. It appears that the thermodynamic quantities which determine the course of the melting curve are the differences of compressibility, thermal expansion, and specific heat (C_p) between solid and liquid. We cannot in general determine all three of these quantities from the data already given for the melting curves, but if one of them can be determined in some other way, there are relations which determine the other two. In some cases, at atmospheric pressure, the data are at hand from which all three of these quantities may be determined. Furthermore, at high pressures, it is shown that certain inequalities hold, in virtue of which we are able to make an estimate of the difference of compressibility between solid and liquid which is correct to perhaps 30 per cent. These very rough values for the difference of compressibility are given and discussed.

There are also now at hand data sufficient to allow the comparison of substances of chemically similar constitution; for instance, CCl_4 with $SiCl_4$, or $CHCl_3$ and $CHBr_3$. Some attention is given to the question as to whether the melting curves show any regularly varying behavior with chemical substitutions of this nature.

It must be recognized, however, that any purely thermodynamic discussion cannot carry us very far on our way. What we are searching for ultimately is a description of the construction of the atom so detailed that we can describe how the atoms are put together in a crystal, and how and why they fall apart when they melt. We are very far indeed from such a goal.

The apparatus was the same as that used in the first paper, and the methods of computation are similar. The tables are somewhat fuller, the values of $d\tau/dp$ being included, and the values of the melting temperatures have been smoothed so as to give differences regular to tenths of a degree. In the preceding paper the equilibrium temperatures were read directly from the curves without further smoothing, so there were irregularities in some cases of several tenths of a degree. These irregularities did not affect the values of $d\tau/dp$, however, which were determined and smoothed in another way. The values of ΔV, $d\tau/dp$, and ΔH given in the tables may not always be exactly related by the thermodynamic equations; this is because these three quantities were smoothed independently, after the calculations had been made. Any such discrepancy, however, is always much less than the probable error with which any of these quantities may be determined.

The data for the individual substances follow.

DETAILED DATA FOR NINE SUBSTANCES.

Bromoform.—Specimens of bromoform from two different sources were used. The first was from Eimer and Amend. It was purified by fractional distillation and crystallization at 0°. There was initially some slight amount of volatile impurity present as shown by the fact that boiling began at 60°, but the boiling point very rapidly rose to 148° and remained there while four fifths distilled. The recrystallized substance was slightly yellow, but had a nearly constant melting point at 7.78°. Five points were determined with this sample, between 900 and 7,000 kgm. This sample was lost by an accident to unrelated parts of the apparatus, when only two more points were necessary for the completion of the curve at high pressures. A fresh lot was ordered from Eimer and Amend, but although this was purified by exactly the same process as the first, the impurity remaining was too large for satisfactory results. Another lot was then obtained from the J. T. Baker Chemical Co., made especially to order. This was further purified by the process above, but could not be obtained as pure as the first lot. It melted over a temperature range 0.4° wide, the maximum melting point being 7.62°. The corners of the melting curve were, therefore, somewhat rounded, but not so much as to prevent satisfactory results. The points at nearly atmospheric pressure and the two highest pressure points were determined with this sample. From 40 to 44 gm. were used.

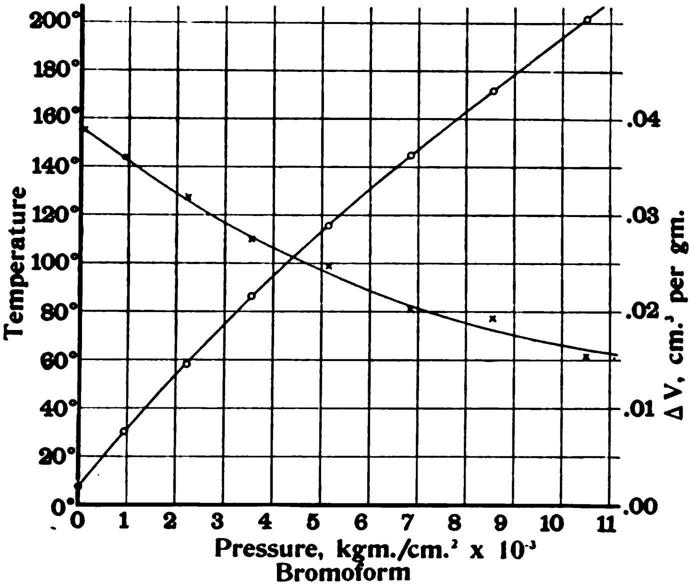

Fig. 1.

Bromoform. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

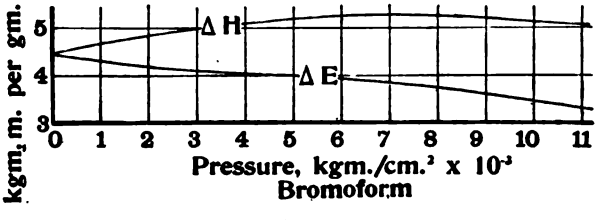

Fig. 2.

Bromoform. The computed values for the latent heat and the change of internal energy when the solid melts to the liquid.

The second set of measurements was made at an interval nearly six months after the first, with a different manganin coil. The $p - t$ points of the second set fit in smoothly with those of the first set, and the

ΔV points of the two sets are consistent within the limits of error, which are here somewhat larger for ΔV than usual. The experimental results are shown in Fig. 1, the computed values of ΔH and ΔE in Fig. 2, and a summary of the numerical values in Table I.

Table I.

Bromoform.

Pressure.	Temperature.	ΔV Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	° 7.78	0.03906	.0245	4.477	4.477
1,000	31.5	355	230	4.699	4.344
2,000	53.8	322	217	4.852	4.208
3,000	74.9	292	204	4.982	4.106
4,000	94.7	266	192	5.097	4.033
5,000	113.3	243	180	5.217	4.002
6,000	130.8	221	170	5.252	3.926
7,000	147.3	203	162	5.267	3.846
8,000	163.2	188	1565	5.242	3.738
9,000	178.7	176	1535	5.151	3.576
10,000	194.0	166	1515	5.118	3.458
11,000	209.1	157	1500	5.047	3.320

There are several other determinations of the melting point at atmospheric pressure. The earliest is by Thorpe,[2] 2.5°, for what must have been a very impure specimen. Later and better determinations are 7.6° by Steudel,[3] 7.8° by Perkin[4] and 7.5° by Feist and Garnier.[5] The highest of these values, that by Perkin, is in essential agreement with that found above. Perkin remarks at some length on the difficulty of obtaining pure bromoform. He says that it decomposes somewhat on distillation, and that the best method of purification is by repeated crystallization. The density of liquid bromoform is given by Thorpe as 2.8341 at 0° and 2.81165 at 8.56°; by Perkin as 2.90246 for $D_{15}{}^{15}$ and 2.88253 for $D_{25}{}^{25}$, and 2.895 by Feist and Garnier. There seem to be no determinations of the latent heat or the crystalline form.

At room temperature and at 200° no new forms were found between the melting curve and 12,000 kgm. It has been shown by Wahl,[6] however, that at atmospheric pressure there is another modification at low temperature. The reaction to the new form runs only in a narrow interval; the ordinary form may be readily subcooled into a region where

[2] T. E. Thorpe, Jour. Chem. Soc., Vol. 37, 141–225, 1880.

[3] V. Steudel, Wied. Ann., *16*, 369–394, 1882.

[4] W. H. Perkin, Jour. Chem. Soc., Vol. 45, 421–580, 1884.

[5] K. Feist und Ch. Garnier, Arch. Pharm., *249*, 458–463.

[6] W. Wahl, Proc. Roy. Soc., Vol. 89, 331, 1913.

the reaction to the new form does not run. At high pressures the viscous resistance to the reaction increases, and this may be the reason for my failure to find the new form. However, Wahl does not state the temperature of the transition, and as we have no idea whatever as to the magnitude of the change of volume or the latent heat, one cannot tell whether any part of the region investigated above contains the region of stability of the new form.

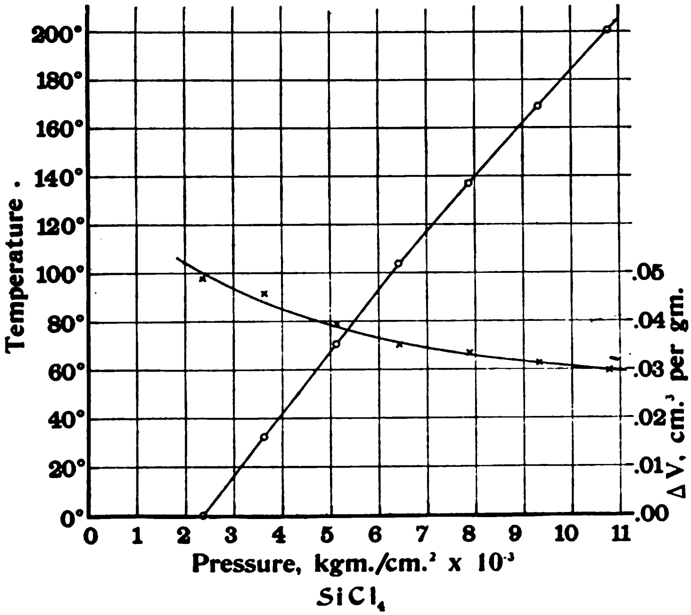

Fig. 3.

Silicon tetrachloride. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

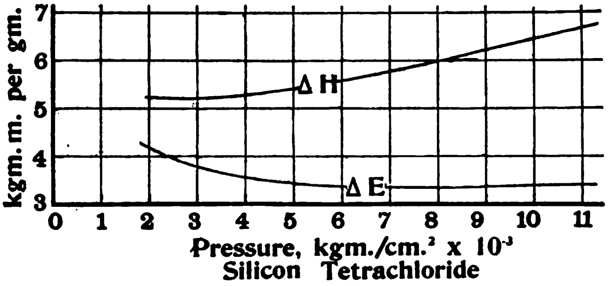

Fig. 4.

Silicon tetrachloride. The computed values for the latent heat and the change of internal energy when the solid melts to the liquid.

Silicon Tetrachloride.—Measurements were made on only one sample of

$SiCl_4$. This was Kahlbaum's; it is supplied in sealed glass tubes, and was perfectly colorless. No attempt was made to further purify it, as this would require considerable chemical skill, because of its spontaneous decomposition on contact with moist air. The freezing was, nevertheless, gratifyingly sharp, much sharper than appeared likely with a substance of this nature. 21 g. were used.

The experimental results are shown in the curves of Fig. 3, the computed values of ΔH and ΔE in Fig. 4, and the numerical values in Table II.

TABLE II.

Silicon Tetrachloride.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M. Gm.	Change of Energy Kgm. M./Gm.
	°				
2,000	−10.0	.0522	.0273	5.23	4.19
3,000	+16.7	470	263	5.20	3.79
4,000	42.6	428	256	5.28	3.57
5,000	67.9	395	2485	5.42	3.44
6,000	92.5	368	241	5.56	3.35
7,000	116.3	347	234	5.78	3.35
8,000	139.4	330	228	5.97	3.33
9,000	161.8	317	222	6.23	3.38
10,000	183.8	306	217	6.44	3.38
11,000	205.4	297	213	6.67	3.41

Apparently very few measurements have been made on this substance I have found only one value for the melting point, − 89°, quoted in Kaye and Laby's tables from a source not mentioned. But this value must have been obtained from a very impure specimen, because it lies considerably below any value that the curve above would extrapolate to. It has seemed best, therefore, in Fig. 3 not to try to run the melting curve below 2000 kgm. An unforced extrapolation of the melting curve would give − 67° for the melting point at atmospheric pressure. It would probably be safe to accept this, in lack of other experiments, as a better value than − 89°.

No other modifications of the solid were found to 12,500 kgm. at 30° and to 12,400 kgm. at 200°. This was a disappointment, as I had expected other modifications in analogy with CCl_4; in fact this was the only reason for undertaking the investigation of this substance.

Monochlorbenzol.—This was Kahlbaum's purest, further purified immediately before use. The middle third of the distillate obtained with a Hempel fractionating column proved to be sufficiently pure. Seven points on the melting curve were obtained with this substance, all with the same filling of the apparatus. That the purity was sufficient, is shown by the ΔV points, which are fully as regular, if not more so, than usual. 17 gm. were used.

The experimental results are shown in Fig. 5, the computed values of ΔH and ΔE in Fig. 6, and the numerical values in Table III.

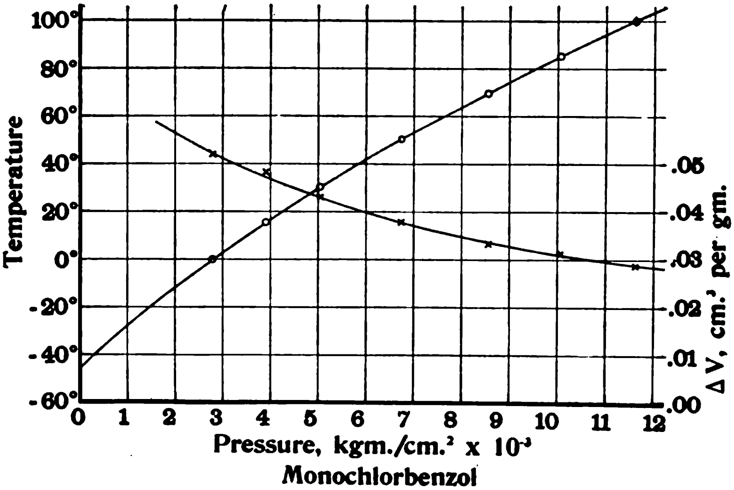

Fig. 5.

Monochlorbenzol. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

Very recently, in fact since the measurements above were made, the melting point of CH_5Cl has been determined with particular care at atmospheric pressure by Henning,[7] for use as a fixed point in low temper-

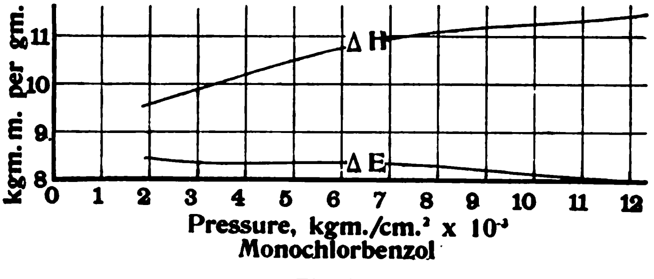

Fig. 6.

Monochlorbenzol. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

ature thermometry. His value is − 45.5°. This lies very well on the curve passing through the points found above at high pressures. Previous values of the melting point were − 40°, given by Béhal and Valeur,

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[7] F. Henning, Ann. Phys., Vol. 43, 282–294, 1914.

Table III.

Monochlorbenzol.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	−45.5		.0184		
1,000	−28.0		167		
2,000	−12.0	.0565	154	9.58	8.45
3,000	+ 2.9	511	1425	9.90	8.36
4,000	16.7	469	133	10.22	8.34
5,000	29.7	432	125	10.47	8.31
6,000	41.9	400	117	10.76	8.36
7,000	53.3	372	111	10.93	8.33
8,000	64.0	349	106	11.10	8.31
9,000	74.4	328	102	11.18	8.23
10,000	84.5	311	099	11.24	8.13
11,000	94.2	297	0965	11.31	8.04
12,000	103.6	285	094	11.42	8.00

− 45° by Schneider,[8] and − 44.9° by Haase.[9] These figures are interesting, because without other evidence one is always inclined to accept the highest listed value of a melting point as most probably accurate,

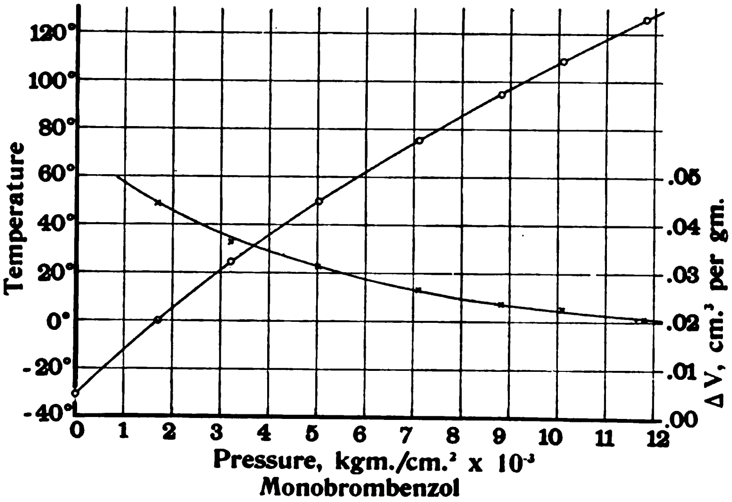

Fig. 7.

Monobrombenzol. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

lower values being explained by impurities, whereas here, the more recent and more accurate values are lower. For the density we have by

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[8] B. V. Schneider, ZS. phys. Chem., *22*, 225–240, 1897.

[9] E. Haase, Ber. D. Chem. Ges., *26*, 1052–1054, 1893.

Adrieenz[10] 1.1284 at 0° and 1.1052 at 21.69°, and by Biron[11] 1.1279 at 0° and 1.1064 at 20°. There seem to be no determinations of the latent heat or the change of volume at atmospheric pressure or of the crystalline form. An extrapolation of the above values for ΔV, assuming constant second differences, gives 0.0711 cm.³/gm. Corresponding to this is the value 8.77 kgm.m./gm. or 19.7 cal./gm. for the latent heat.

At 30° and at 100° no new modification of the solid was found to 12,800 kgm. From analogy with benzol, it would not have been surprising if there had been a second form.

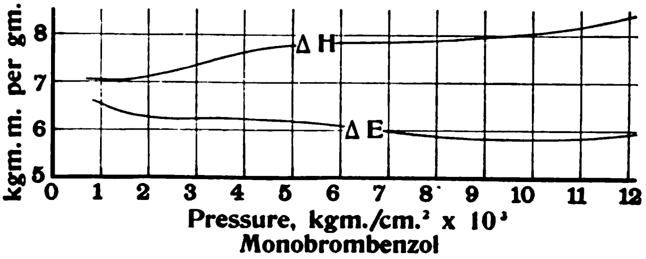

Fig. 8.

Monobrombenzol. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

Monobrombenzol.—Like monochlorbenzol, this was Kahlbaum's purest, and was further purified by fractional distillation. The purity is sufficient as evidenced by the regularity of the points. Seven points were obtained, all with the same filling of the apparatus. 23 gm. were used.

TABLE IV.

Monobrombenzol.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	−31.1		0.0197		
1,000	−12.1	0.0486	181	7.010	6.524
2,000	5.3	428	167	7.134	6.278
3,000	21.3	382	1525	7.375	6.229
4,000	35.9	345	140	7.615	6.235
5,000	49.4	315	131	7.756	6.181
6,000	62.0	288	123	7.845	6.117
7,000	74.1	266	118	7.827	5.965
8,000	85.7	248	114	7.868	5.868
9,000	96.9	234	109	7.943	5.837
10,000	107.6	222	105	8.050	5.830
11,000	117.9	212	102	8.127	5.795
12,000	127.9	205	098	8.389	5.929

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[10] A. Adrieenz, Ber. D. Chem. Ges., *6*, 441–444, 1873.

[11] E. Biron, Jour. russ. phys. Chem. Ges., *42*, 135–166.

The experimental results are shown in Fig. 7, the computed values of ΔH and ΔE in Fig. 8, and the numerical values in Table IV.

For the melting point at atmospheric pressure we have − 30.5° by Schneider,[8] − 30.7° by Bugarsky,[12] and − 31.3° by Haase.[9] Here, as in the case of chlorbenzol, the lower value, − 31.3°, seems to be probably more accurate, since the curve extrapolates to this without any initial abnormalities in $d\tau/dp$. For the density of the liquid Biron[11] gives 1.5223 at 0° and 1.4953 at 20°, Adrieenz[10] 1.5177 at 0° and 1.4898 at 20.96°, and Wagner[13] 1.5203 at 0° and 1.4945 at 20°. There seem to be no values of change of volume or of latent heat for comparison at atmospheric pressure. We may extrapolate from the values of Table IV. and find at atmospheric pressure 0.0564 cm.^{3}/gm. for the change of volume, and 7.0 kgm. m./gm. for the latent heat. There are apparently no other measurements for comparison at high pressures. The crystalline form has not been determined.

At 25°, no new modification of the solid was found to 12,500 kgm., and at 126°, no new form to 12,700 kgm.

Benzophenone.—This substance was obtained from Eimer and Amend, and was further purified by crystallization at constant temperature in the thermostat. The temperature was so adjusted that crystallization took place very slowly, during 48 hours. Large perfect crystals were obtained. 13 to 18 gm. were used.

Various accidents made necessary measurements at four different times with four different fillings of the apparatus. The benzophenone was placed in an inverted nickel steel shell, instead of the bulb used for substances liquid at room temperature. This shell will be further described in the next paper dealing with solids. With the first filling of the apparatus a complete series of measurements was made over the entire pressure range, but on taking the apparatus apart it was found that the shell had split at some time during the application of pressure, allowing some of the benzophenone to escape. On working up the results, an abrupt drop in the values of ΔV showed that the precise point at which this had taken place was after the determination of the first point. The splitting of the nickel steel shell seems to have been caused by a quite unusual rigidity of this substance under pressure. Of course the values of pressure and temperature found during this first run were quite unaffected by the escape of some of the material; it was the ΔV values that had to be discarded, only the first being good. The second filling was made for a determination of the point at nearly atmospheric pressure;

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[12] Bugarsky, Math. u. Naturw. Ber. aus Ungarn, *26*, 89–151, 1910.

[13] F. Wagner, Lieb. Ann., *221*, 61–107, 1883.

this was accomplished without incident and with unusually sharp freezing. The third filling of the apparatus gave three points with good values of ΔV at 1,200, 3,200 and 2,200 kgm. This set of readings was terminated by the breaking of the lower cylinder into two cleanly divided halves, a rather unusual fracture. Apparently it had been started by an explosion some time previously. The fourth set of readings gave the two points needed to complete the curve at the highest pressures. The data given amount, then, to a double determination of the coördinates of the melting curve, and a single determination of the course of the ΔV curve, but with four different fillings of the apparatus, with different quantities of material.

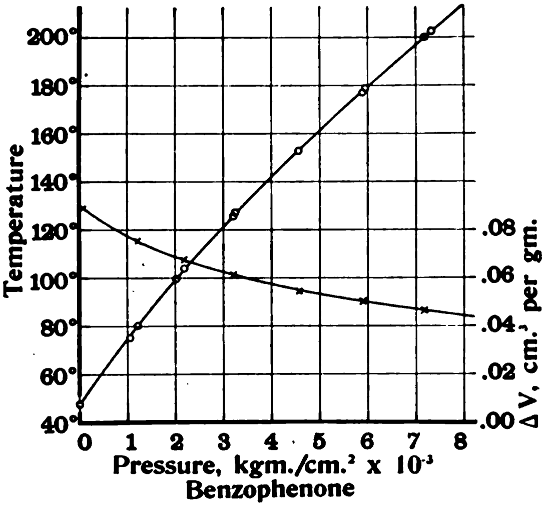

Fig. 9.

Benzophenone. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

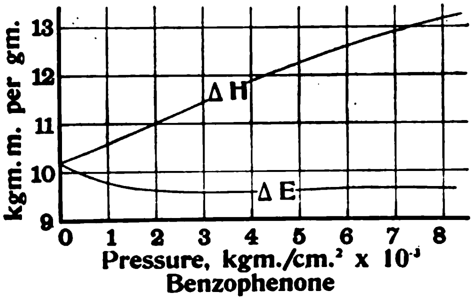

Fig. 10.

Benzophenone. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

The experimental results are given in Fig. 9, the computed values of ΔH and ΔE in Fig. 10, and the numerical values in Table V.

TABLE V.

Benzophenone.

Pressure.	Temperature.	ΔV Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	° 47.77	0.0904	.02845	10.20	10.20
1,000	74.6	773	2545	10.56	9.79
2,000	98.9	689	2330	11.00	9.62
3,000	121.3	624	2145	11.48	9.61
4,000	142.0	571	2000	11.85	9.57
5,000	161.3	532	1885	12.26	9.60
6,000	179.6	498	1785	12.63	9.64
7,000	197.0	468	1705	12.90	9.62
8,000	213.7	442	1635	13.17	9.63

There are a number of values for comparison. For the melting point, Tammann[14] gives 48.11° in Kristallisieren und Schmelzen, 47.7° in 1898, and 48.5° in 1899. Linnemann[15] gives 48° to 48.5°, Bruner[16] 48.0°, Hulett[17] 48.10°, and Block[18] 48.1°. The value found directly for the sample above, 47.77°, is evidently too low; the best value selected from the above is probably about 48.11°. For the change of volume Tammann[19] gives 0.0875 to 0.0883 cm.^{3}/gm., and Block[18] 0.0877 against 0.0904 above. For the latent heat, Tammann[19] gives 23.4 from a direct determination and 23.95 cal. calculated from the coördinates of the melting curve. Eykmann[20] determines it as 23.2 from the depression of the freezing point, and Bruner[16] gives the value 23.7. The value that I found above was 23.9; the agreement of all these values is closer than usual. The melting curve found by Tammann at high pressures lies somewhat below that given above, the discrepancy increasing as usual with increasing pressure, but the difference is somewhat less than usual. At 90° my pressure is 20 kgm. lower than his; at 100°, 60 kgm. lower; and at 130°, 160 kgm. lower. Tammann's values for ΔV also drop off with increasing pressure more rapidly than do mine, but the discrepancy is not so much as for many other substances. In addition to Tammann, Hulett[17] has also

[14] G. Tammann, "K. und S.," p. 229. Wied. Ann. *66*, 491, 1898. ZS. phys. Chem., *29*, 51–76, 1899.

[15] Ed. Linnemann, Lieb. Ann., *133*, 1–32, 1865.

[16] L. Bruner, ZS. Chem., *4*, 497–519, 1899.

[17] G. H. Hulett, ZS. phys. Chem., *28*, 629–672, 1899.

[18] H. Block, ZS. phys. Chem., *78*, 385–425, 1912.

[19] G. Tammann, "K. und S.," p. 231.

[20] J. F. Eykmann, ZS. phys. Chem., *4*, 497–519, 1889.

determined the effect of pressure on the melting point up to 300 kgm. His values agree with mine better than with Tammann's. Thus for the initial slope, $d\tau/dp$, Tammann gives 0.0276, Hulett 0.0289, and I find 0.02845.

At 30°, I found no new modification to 12,000 kgm., and at 200° none to 12,500. This result is an interesting one in view of the well known tendency of benzophenone to crystallize in other forms at atmospheric pressure. At least three other, unstable, forms are known at atmospheric pressure. The existence of these unstable forms seems connected in some way with the rather unusual amount of subcooling that benzophenone will allow. If it is allowed to crystallize from the subcooled condition it is likely that an unstable form will appear, rather than the normal stable form. Now in these experiments at high pressures, in which freezing was produced by increasing pressure at constant temperature, it was often necessary to push the pressure considerably beyond the equilibrium value, that is, to produce considerable subcooling, before crystallization could be induced. Yet never did any other than the normal crystal appear, although analogy with the behavior at atmospheric pressure would lead one to expect the sporadic occurrence of unstable forms. The amount of superpressure necessary to produce solidification varied capriciously, as is to be expected, and might be rather large. Once, at 179°, 450 kgm. superpressure was necessary, at 80°, 1,500 kgm., and again at 177°, 2,600 kgm. These values correspond to 9°, 34°, and 46° subcooling. No serious effort was made to obtain regular values for the subcooling; doubtless better values could be found, but there must always be an element of caprice about anything of this kind.

There may be two reasons for the failure ever to observe any of the unstable forms. Tammann has noticed that the unstable forms are much more difficult to produce and that they change spontaneously to the stable form much more readily when there is a metal in contact with the benzophenone than when only glass is used. For these experiments contact with some metal, mercury to transmit the pressure if nothing else, is unavoidable, so that the conditions are never favorable to the appearance of unstable forms. In the second place, there may of course be a specific temperature or pressure effect, the unstable nuclei being less likely to form at the high temperatures. This is not unlikely, and is somewhat borne out by the tendency, in a rough way, for the possible subcooling to become less at high temperatures. At atmospheric pressure, for instance, a subcooling of 100° is possible under the proper conditions. On the whole, then, the chances seem unfavorable for the study of the unstable forms under pressure. No very serious attempt was made to do this in the present work, but it is significant that F. Körber,[21] one of Tammann's pupils, in a recent investigation of the effect of pressure on unstable forms, has not included benzophenone in his list of substances.

The same sluggishness that is manifested in the large amount of possible subcooling has also made possible a rough qualitative examination of the velocity of crystallization under pressure. This is not possible for most substances, because the heat of reaction is the dominating factor for those substances with a normal rate of crystallization, the crystallization proceeding as fast as the heat of reaction can be conducted away through the walls of the pressure cylinder. A consequence of this is that for most substances the melting when the solid is superheated takes place as rapidly as the freezing when the liquid is subcooled in the presence of the solid. The velocity of these reactions is indicated very simply by the rate at which pressure returns to its equilibrium value after it has been displaced to the one side or the other. But with benzophenone the velocity of crystallization is so slow that the heat of reaction has a chance to be dissipated rapidly enough not to entirely mask the normal progress of the reaction. It has been possible to establish the fact for benzophenone that the velocity of crystallization is very much less than that of melting. Careful measurements were made of the rate of spontaneous recovery of pressure from above and below at five different temperatures. Figure 11 reproduces one of these curves for the reaction velocity from above and below. The greater speed of melting is shown by the sharper corner

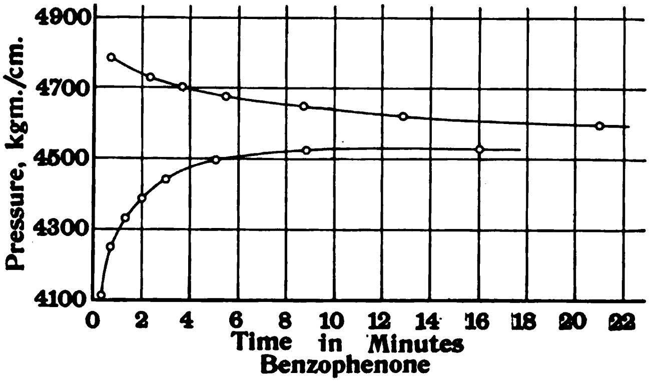

Fig. 11.

Benzophenone at 152°. Shows the recovery of pressure, when pressure has been displaced from the equilibrium value, plotted against time. On the rising curve, the solid is melting, and on the falling curve the liquid is crystallizing. Note that the rate of melting is more rapid than that of crystallization. In the actual experiment, the melting curve was obtained first; in the diagram the freezing curve has been displaced in time for convenience of comparison.

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[21] F. Körber, ZS. phys. Chem., *82*, 45–55, 1913.

of the curve. An examination of all five curves shows that the velocity of melting does not vary markedly with temperature, indicating no large variation in thermal conductivity with rising temperature and pressure along the melting curve. But it does seem probable, although it is not entirely certain, that the velocity of crystallization increases with rising temperature. Because of the impossibility of superheating a solid, the velocity of melting will, of course, always be determined essentially by the heat conductivity of the walls. Irregularity in measurements of this kind is to be expected. For example, if it happened that at higher temperature the crystallization grew from one chance nucleus, while at low temperatures there were two, then the rate of recovery at low temperatures might be greater, although the actual velocity of crystallization might be less. The question of reaction velocity will be considered at greater length in a future paper of this series.

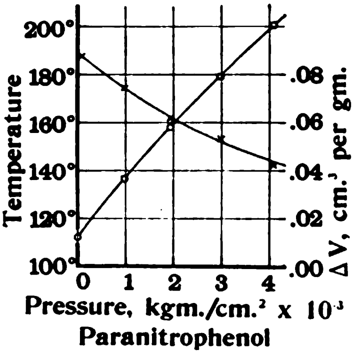

Fig. 12.

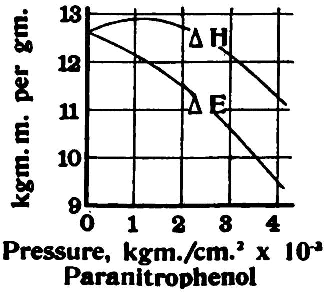

Fig. 13.

Paranitrophenol. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

Paranitrophenol. The computed values of the latent heat, and the change of internal energy when the solid melts to the liquid.

Paranitrophenol.—Merck's " blue label " preparation was used without attempt at further purification. There was considerable impurity present as shown by the low value of the freezing point and the rounding of the corners of the melting curve. In fact, this is one of the most impure of the substances for which data are given here. Error from the rounding of the corners of the melting curves was largely avoided, however, by running the pressure an unusual distance beyond the freezing point, allowing a better extrapolation.

Two sets of measurements were made; one comprised points at four pressures above 900 kgm., and the other was the usual measurement with the low pressure apparatus at approximately atmospheric pressure. The quantities used were 15.7 and 20.0 gm. respectively.

The observed points are shown in Fig. 12, the computed values of ΔH and ΔE in Fig. 13, and the numerical values in Table VI.

TABLE VI.

Paranitrophenol.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	112.4	.0891	.02720	12.63	12.63
500	125.5	812	2524	12.82	12.41
1,000	137.7	740	2356	12.90	12.16
1,500	149.1	674	2208	12.89	11.88
2,000	159.8	614	2090	12.72	11.49
2,500	170.0	564	2000	12.49	11.08
3,000	179.8	520	1940	12.14	10.58
3,500	189.4	480	1894	11.71	10.03
4,000	198.8	445	1866	11.26	9.48

The normal melting point of this substance is given as high as 115° by the Chemiker Kalendar, but the authority is not stated. The melting point is given as 114° by Schiff,[22] 114° by Wagner,[23] and 111.46° by Mills.[24] The value found above, by an extrapolation of the value at 80 kgm., was 112.4°. For the density of liquid nitrophenol, Schiff[22] gives the formula $1.2809 - 0.00095\,(t^\circ - 114)$, and for the density of the solid at room temperature Schroeder[25] gives 1.468. Assuming the value found above for ΔV, this gives 0.00015 as the value of the mean dilatation of the solid between room temperature and the melting point. At high pressures there are no previous measurements for comparison.

No new modification of the solid was found to 12,000 kgm. either at room temperature or at 200°. The region between atmospheric pressure and 2,000 kgm. was investigated with rather more than usual care at room temperature. The chief reason for undertaking the investigation of this substance at all is that it is usually listed as one with two modifications at atmospheric pressure; in fact the recent Tables of the Société Française marks this substance with an asterisk as a particulary striking example of a polymorphic transition. The low temperature form is supposed to be a bright pink which changes to a nearly colorless form on warming. This is usually stated on the authority of Lehmann;[26] he is sometimes quoted as saying that this transition is enantiotropic and sometimes as monotropic. His original statement is monotropic. In the Tables of the French Society his unstable and stable forms have been interchanged. In an attempt to determine whether there is a transition at low pressures, perhaps unaccompanied by a change of color, dilatometric measurements were made in the low pressure apparatus at a constant pressure of 80 kgm. No perceptible volume change could be found between 30° and the melting point.

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[22] R. Schiff, Lieb. Ann., *223*, 247–268, 1884.

[23] P. Wagner, Ber. D. Chem. Ges., *7*, 76–78, 1874.

[24] E. J. Mills, Phil. Mag. (5), Vol. *14*, 1–29, 1882.

[25] A. Schroeder, Ber. D. Chem. Ges., *12*, 561–567, 1879.

[26] O. Lehmann, ZS. Kryst., *1*, 43–48, 1877.

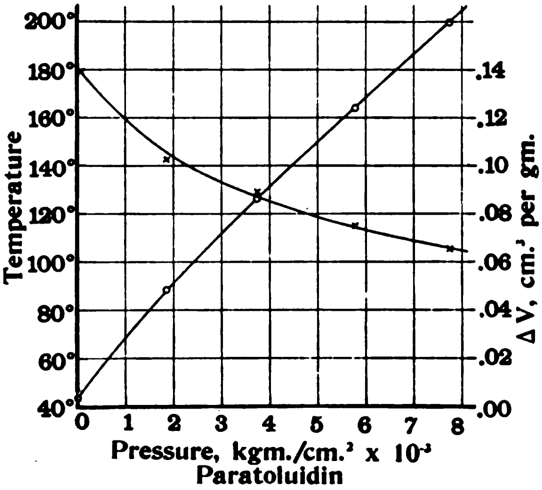

Fig. 14.

Paratoluidin. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

Paratoluidine.—This substance was obtained from Eimer and Amend, and was purified by crystallization at constant temperature in the thermostat. Crystals in the form of needles several inches long were obtained. The impurity shown by the rounding of the corners was, however, somewhat more than usual. To avoid errors from this cause in

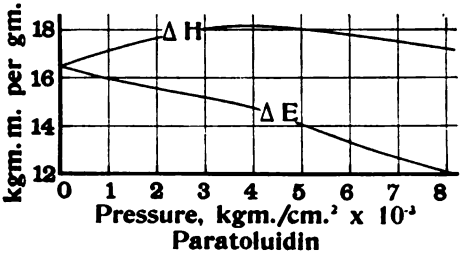

Fig. 15.

Paratoluidin. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

the ΔV determinations, measurements were usually begun 1,500 kgm. beyond the melting point. Only two sets of measurements were made; one of four points at high pressures, and one at 80 kgm. In addition, the melting point was determined at atmospheric pressure. The quantities used were 12 and 16 gm.

The experimental results are shown in Fig. 14, the computed values of ΔH and ΔE in Fig. 15, and the numerical values in Table VII. Especially noteworthy is the rapid approach to linearity of the melting curve at the higher pressures, and the unusually large volume change at atmospheric pressure.

TABLE VII.

Paratoluidine.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	43.6	.1413	.0271	16.51	16.51
1,000	69.0	.1195	238	17.17	15.97
2,000	91.5	.1037	214	17.66	15.59
3,000	112.0	.0931	1977	18.04	15.25
4,000	131.3	.0852	1894	18.19	14.78
5,000	150.0	.0789	1854	18.01	14.06
6,000	168.4	.0736	1831	17.74	13.32
7,000	186.6	.0688	1810	17.48	12.66
8,000	204.6	.0647	1794	17.22	12.04

The melting point at atmospheric pressure of the specimen used above was 43.6°. The Chemiker Kalendar gives 45° for the melting point, but the authority is not cited; probably this is from Brühl.[27] Other values for the melting point are 38.90° by Batteli,[28] 42.89° by Mills,[24] 43.3° by Tammann,[29] 43.73° by Hulett,[17] and 38.7° by Block.[18] The value of Hulett seems to be the best. For the latent heat we have the following values. O. Pettersson[30] gives 37.3 cal. as recomputed by Tammann from Pettersson's value 35.8 at 31° so as to reduce to the melting point. Tammann[29] calculates from his own data 35.6 cal. for the latent heat. Batteli[28] gives 39.3, Eykmann[20] finds 38.6, and I find by calculation from my own data 38.7 cal. For the density Rüdorff[31] gives 1.046 at room temperature, and Brühl[27] 0.9538 for the liquid at 59.1°. For the change of volume, Batteli[28] gives 0.066 cm.³/gm., and Block[18] 0.0877 at atmospheric pressure, against my value 0.1413 above. Tammann[29] gives one

[27] J. W. Brühl, ZS. phys. Chem., *16*, 193–225, 1895.

[28] A. Batteli, R. Ist. Ven. (6), *3*, 1781–1811, 1884–85.

[29] G. Tammann, "K. und S.," p. 240.

[30] O. Pettersson, Jour. prak. Chem., *24*, 129–168, 1881.

[31] Fr. Rüdorff, Ber. D. Chem. Ges., *12*, 249–252, 1879.

value under pressure, 0.115 at 575 kgm. against 0.1283 above. There must have been some blunder in the values of Batteli and Block, because they would give impossibly low values for the latent heat when combined according to Clapeyron's equation with the values of $d\tau/dp$, in which Tammann, Hulett, and I are in essential agreement. Tammann has determined the coördinates of the melting curve to 3,000 kgm. At 1,000 kgm. his value is 1.3° lower than mine, at 2,000, 2.1° lower, and at 3,000, 3.6° lower. Hulett[17] also measured the effect of pressure on the melting curve up to 300 kgm. His initial value of $d\tau/dp$ is 0.0270 against 0.0271 above.

No new modifications of the solid were found up to 12,000 kgm., either at room temperature or 200°.

Methyl Oxalate.—It is a matter of considerable difficulty to obtain this substance pure, and it was necessary to make several attempts. The first sample was from Eimer and Amend, made especially to my order, and as furnished by them had a melting point of 48°. It was further purified by distilling in air at atmospheric pressure and crystallizing in the thermostat; this raised the melting point to 52.96°. The melting point of the pure substance is listed as 54°. With this sample three points on the melting curve were obtained between 35° and 175°, and also the change of volume at low pressures. There was considerable rounding of the corners of the melting curve, but the results showed conclusively that there was no second modification, a point which will be touched on again later. The series of runs with the first sample was discontinued because of accidental loss of all the purified substance. Another sample, obtained from the ordinary stock of the Harvard Chemical Laboratory, had a melting point of 49°, but no attempt was made to further purify it. A second lot was then obtained from Eimer and Amend, but the same process of purification as that applied to the first sample did not yield a product with so high a melting point. Part of the impurity in these first samples was probably introduced by the process of distillation; it seems certain that some decomposition is caused by heating to 163°, the boiling point at atmospheric pressure. Finally, a special sample was made at the Harvard Chemical Laboratory under the direction of Professor Kohler. The method was not an uncommon one; esterification of pure anhydrous oxalic acid, using pure methyl alcohol and a small quantity of pure sulfuric acid. Especial pains was taken to start with pure reagents; Professor Kohler tells me that it is very difficult to remove the impurities if they have once got into the methyl oxalate, but that one must have purity from the start. This sample came in the form of flakes, which were quite dry and not adherent to each other, whereas the other samples had been obviously impure with some slight moisture. The great purity of this specimen is shown by its high melting point, 54.14° at atmospheric pressure when half melted, as

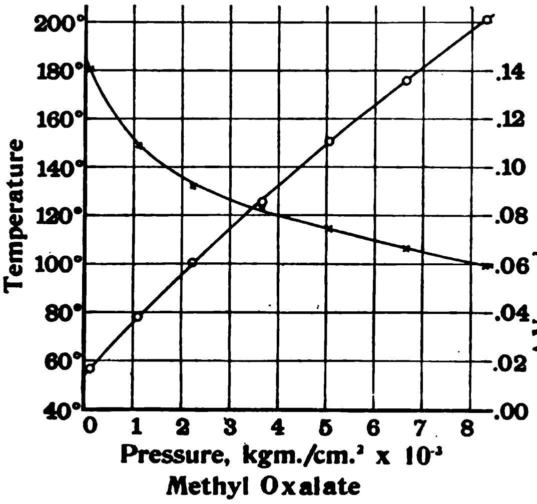

Fig. 16.

Methyl oxalate. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures and the crosses the observed changes of volume.

obtained by extrapolation from the melting point at 100 kgm. This seems to be somewhat higher than any value previously listed. This melting point can be counted on with some certainty, because at 100 kgm.

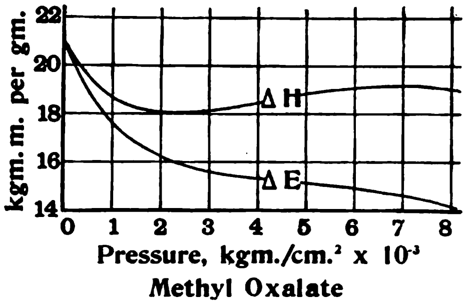

Fig. 17.

Methyl oxalate. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

it was possible to shut the equilibrium pressure within two values differing by only 3 kgm., the equivalent of 0.07°, when approached from above and below. There was, nevertheless, some slight impurity in this best sample, because it was possible to detect a slight rounding of the corners. At

80 kgm., where the true melting temperature is 56°, this rounding was perceptible at 50°, but was imperceptible at 45°. In this connection it may pay to emphasize the very delicate criterion of impurity afforded by the rounding of the corners. At 50°, the rounding was such as to amount to a premature melting of 0.0082 of the total quantity. This would mean a total depression of the freezing point, if the impurity were uniformly distributed throughout the mass, of 0.10°. We may, therefore, assume 54.24° as the most probable melting point of the absolutely pure substance at atmospheric pressure. The rounding of the corners became somewhat greater at the high pressure end of the melting curve. Evidently the high temperature caused some decomposition under pressure, just as it does when distillation is attempted at atmospheric pressure. The rounding was not large, however, and should not affect appreciaby the correctness of the values for equilibrium pressure and temperature, and only slightly the values for the change of volume.

Two runs, with two different fillings of the apparatus were made; one for all the points at high pressures, and the other for the one point at low pressure.

The experimental values for equilibrium pressure and temperature and the changes of volume are shown in Fig. 16, the computed values of latent heat and change of internal energy in Fig. 17, and the numerical values are collected in Table VIII. In this table the equilibrium temperatures have been corrected by adding 0.10° to the observed temperatures, this correction being obtained from the data above for the rounding of the corners at 77 kgm., and using the assumption that the depression does not change markedly with pressure. The legitimateness of this assumption has been discussed in the first paper of this series.

TABLE VIII.

Methyl Oxalate.

Pressure.	Temperature. °	ΔV Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	54.24	0.1453	.02261	21.03	21.03
1,000	75.8	.1115	2078	18.71	17.60
2,000	95.8	.0957	1946	18.13	16.22
3,000	114.7	.0862	1838	18.19	15.60
4,000	132.6	.0798	1747	18.52	15.33
5,000	149.6	.0745	1669	18.87	15.14
6,000	165.9	.0696	1601	19.08	14.90
7,000	181.6	.0650	1544	19.14	14.59
8,000	196.8	.0606	1496	19.03	14.18

The initial rapid decrease of the latent heat is an unusual feature; this accompanies the rapid initial decrease in the change of volume, which may be open to question.

The points obtained with the first impure sample at 135°, 155° and 175°, were all about 5° too low; this is probably to be explained by the escape of some of the methyl oxalate and contamination with the kerosense, as well as by the known initial impurity of the sample. This contamination with kerosene was the accident alluded to above which made necessary the abandonment of this sample; it was not detected until these three points had been measured. The value for the change of volume obtained with the impure substance at low pressure is not affected by the error of the high pressure points, and may be expected to be more nearly correct. This value at 77 kgm. was 0.132 cm.^{3} per gm., which is distinctly lower than that found for the pure sample. This shows the importance of using pure substances if accurate values of the change of volume are expected.

The particular object of working with this substance was that it is one for which Tammann[32] has announced the existence of two modifications. Tammann states that there is a transition point at about 25° at atmospheric pressure; from this point the transition line between the two varieties runs upwards to a triple point at 54.0° and 550 kgm. The domain of existence of Tammann's variety I is, therefore, very restricted in extent. I could find no trace whatever of this supposed second modification. Search was made at 77 kgm. by raising temperature from 13° to the melting point in steps of 5°, and at 40° I could find nothing with increasing pressure to 700 kgm., although Tammann's transition line should be found at 300 kgm. at this temperature. There seems to be little question that this result of Tammann's was due to impurity of his sample, which he states had a melting point from 49.5° to 50.2°. In private correspondence, Professor Tammann has suggested to me that the existence of the second variety may be possible only in the presence of impurity, because cases are known in which an unstable variety is formed only in the presence of impurity. This, however, would demand that Tammann's sample was even more impure than would be indicated by the low value of his melting point. If there really are two modifications, there can be little doubt that the modification of Tammann which is stable over by far the greater portion of his pressure range is identical with the variety which I have measured; that is, Tammann's variety II is the same as that measured above. But Tammann's data would demand that the melting point of II be 46.8° at atmospheric pressure, which would mean that his sample contained enough impurity to depress the freezing point by 7.3°. That there is some grave fault with Tammann's measurements on this substance is further indicated by the fact that the coördinates which he gives for the melting curve are at 3,050 kgm. more than 33° lower than those which I have found. It is impossible to explain this by the effect of any initial impurity; a possible explanation is that the design of Tammann's apparatus was such as to allow contamination by the fluid transmitting pressure.

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[32] G. Tammann, "K. und S.," p. 265.

Besides the values of Tammann, there are several other values for comparison at atmospheric pressure. For the melting point we have 50° by Kopp,[33] 49.5° by Bruner,[34] 51° by Bartoli,[35] 52.5° by Stohlmann,[36] and 54.0° by Weger.[37] These wide variations of melting point emphasize the difficulty of getting this substance pure. For the latent heat, there is one value by Bruner,[34] who gives 18.30 kgm. m. against 21.03 above. Bruner's sample was very impure, as shown by its melting point of 49.5°. The change of volume at atmospheric pressure has been measured by Block,[11] working in Tammann's laboratory. But his sample was also impure, as indicated by the low melting point, 51.4°; the impurity may have been the same as that of Tammann's sample. He gives for the change of volume 0.0813 cm.^{3} per gm., against 0.1453 above. This enormous discrepancy can be due only to impurity, and emphasizes the necessity for having pure samples for determining the change of volume. It is to be remembered that the value which I obtained with the first impure sample was somewhat lower than that found for the pure one.

Bismuth.—Especial interest attaches to the melting curve of bismuth because, apart from the fact that it is an element, it is one of the few substances whose melting is of the ice type, that is, the volume of the solid is greater than that of the liquid. The question of greatest interest is whether there is a second modification of the solid denser than the liquid analogous to ice III. We are also interested to know whether the melting curve is concave downward, whether the change of volume increases along the melting curve, and whether the latent heat diminishes, as it does for the ice I curve. So far as I know, water is the only other substance of this type whose melting curve has been hitherto determined. The melting curve of bismuth has been previously measured by Tammann[38] and by Johnston and Adams,[39] but the pressure range of these

[33] H. Kopp, Lieb. Ann., *95*, 307–356, 1885.

[34] L. Bruner, Ber. D. Chem. Ges., *27*, 2102–2107, 1894.

[35] A. Bartoli, Gazz. Chim. Ital., *24* (2), 156–172, 1894.

[36] F. Stohlmann, Jour. prak. Chem., (*2*), 40, 341–364, 1889.

[37] F. Weger, Lieb. Ann., *221*, 61–107, 1884.

[38] G. Tammann, ZS. anorg. Chem., *40*, 54–60, 1905.

[39] J. Johnston and L. H. Adams, Amer. Jour. Sci., Vol. 31, 501–517, 1911.

investigators was not high enough to enable them to tell the direction of curvature, and they made no measurements of the change of volume, and so, of course, were not able to calculate the latent heat.

The bismuth was Kahlbaum's purest, used without attempt at further purification. The purity of the specimen was not perfect, because there was some rounding of the corners of the melting curve, but it was only slight.

The previous temperature range of this work has been to only 200°, but the melting point of bismuth at atmospheric pressure is about 270°, so that some modification in the temperature bath became necessary. It was found that the same bath liquid, "Crisco," could still be used for the higher temperatures, provided that a tight cover was placed over the tank to prevent the escape of the stifling smoke into the air of the room. The temperature control was the same as before, by means of a mercury in glass thermostat, which regulated the supply of gas. The temperature regulation by the thermostat was not quite so good at the higher temperatures as it was at the lower ones. The variation of temperature was in some cases as high as 0.7°, or it might be as low as 0.2°. The mean of the extreme values was taken as the temperature of the experiment; this must be very close to the true value at the inside of the heavy steel cylinder. A modification of the method of measuring temperature was also necessary, because the Reichsanstalt calibration of the mercury in glass thermometers used in the previous work reached only to 200°. For this purpose a platinum resistance thermometer was used. This was one that had been constructed by Dr. H. M. Trueblood in this Laboratory for use in his measurements of the Joule-Thomson effect in steam. For this work, I calibrated the thermometer again in ice, boiling water, and boiling naphthalene. For the boiling point of naphthalene and the effect of the barometric pressure upon it, the values of Johnston and Adams[40] were used.

Two sets of measurements were made. The first was with a cylinder which had previously developed a flaw, but which had been patched with apparent success. The flaw redeveloped, however, at about 6,000 kgm. so that the cylinder had to be scrapped. On computing the values for the change of volume from this first run, it appeared that there had always been some minute leak at even the lowest pressures, so that the results had to be discarded. The equilibrium points of this first run up to about 6,000 kgm. were consistently 1° higher than those of the second run. The explanation of this is probably connected with the extreme slowness of the reaction. To meet this difficulty a special method of procedure was adopted during the second run. The second run, made with a new cylinder, was over the entire pressure range up to 12,000 kgm. and was successful in every way. It was gratifying to find that the cylinder would stand the maximum pressure at the higher temperature. During the seasoning of the cylinder, the pressure was pushed to 13,000 at 220°.

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[40] L. H. Adams and J. Johnston, Amer. Jour. Sci., Vol. 33. 534–545. 1912.

The reaction, whether melting or freezing, was very slow at the upper end of the curve. Part of the explanation of this is to be found in the small slope of the melting curve and the low latent heat, but this does not seem sufficient to entirely explain the unexpected slowness of the reaction. The appearance was as if the heat conductivity of the cylinder has become very much less at the higher temperatures. Whatever the explanation, a source of error was found here which I have never observed before at the lower temperatures. To explain the possibility of error, let us suppose that pressure has just been decreased so as to carry the liquid into the region of the solid. Freezing takes place with rise of pressure, accompanied with setting free of heat and rise of temperature. If now, before equilibrium has been completely attained, the pressure is artificially raised, we may get the reverse reaction, that is, a fall of pressure, at a pressure that is lower than the true melting pressure at the temperature of the bath, because the temperature of the inside of the cylinder is higher than that of the bath. This gives the appearance of having shut the equilibrium pressure within two limits, at one of which the pressure rises while at the other it falls, whereas the fall of pressure would have taken place only at a higher pressure if temperature had been completely attained. To avoid the error, one must take especial pains to wait for complete equilibrium. But this would require a very long time at the higher temperatures of the range, perhaps three or four hours from one side only. Apart from the tediousness of the operation, the error from slight changes in the bath temperature during this interval would more than counterbalance any other gain in accuracy. Another procedure was adopted therefore. Pressure was first lowered far enough beyond the equilibrium line to ensure the reaction running partly, so that both phases were present in the apparatus. By moving the piston, the pressure was then raised back to nearly the equilibrium value, and then further slight changes made until pressures were found at which the pressure would fall or rise after a change. The advantage is that a very slight amount of reaction can be detected in this way and then the pressure altered in the correct direction, before there is time for much of the heat of melting to be set free. By careful work, the equilibrium point, both from above and below, can be found in less than an hour by this method, and very much more accurately than by waiting for the pressure to automatically restore itself over the entire range.

A very striking change in the reaction velocity was found below 250°. Below this temperature the reaction becomes as rapid as a normal melting reaction for metals in this type of apparatus, and no such special procedure was necessary as above. No marked change in the thermodynamic properties of bismuth takes place at 250°, judging from the melting curve; if the effect is due to a change in the properties of the bismuth, it must be some molecular change too far below the surface to affect the ordinary thermodynamic properties. If the effect is due to the bismuth, it is difficult to understand how other experimenters have been able to get a sharp melting point at atmospheric pressure by observing the arrest point in the cooling curve. It seems very possible that the effect is not one inherent in the bismuth, but may be due to a change in the thermal conductivity of the kerosene or the steel cylinder. The steel was of chrome-vanadium steel; the cylinders in both the preliminary and the final runs were made of this, and the effect was found both times. There may be some molecular change in the steel at this temperature. The manufacturers recommend heating the steel to 270° to draw the temper.

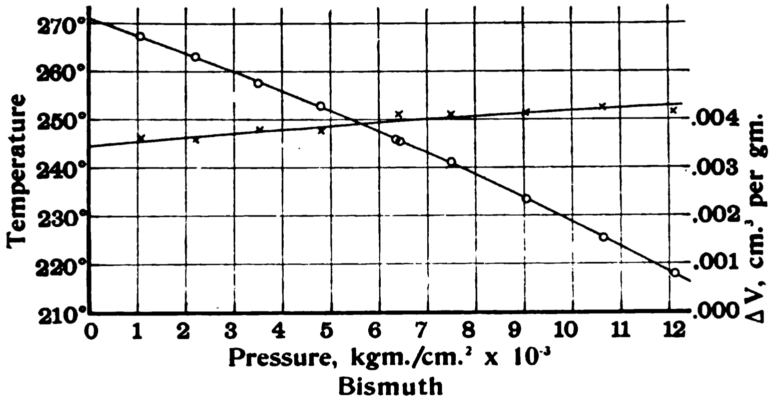

Fig. 18.

Bismuth. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures and the crosses the observed changes of volume.

The observed points and the curves for melting and change of volume are shown in Fig. 18, the computed values for the latent heat and the change of internal energy are shown in Fig. 19 and the numerical values are collected in Table VIII. It is to be noticed that everything is exactly the same as it is for ice I. The melting curve is concave downward, the change of volume curve rises with increasing pressure, and the latent heat and the change of energy become less at the higher pressures. The significance of the rising ΔV curve, unless the dilation relations of solid

Table IX.

Bismuth.

Pressure.	Temperature.	Δv Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat, Kgm. M./Gm.	Change of Energy, Kgm. M./Gm.
1	271.0°	0.00345	−0.00342	5.49	5.49
1,000	267.5	354	357	5.36	5.39
2,000	263.8	362	372	5.24	5.31
3,000	260.0	370	387	5.11	5.22
4,000	256.0	378	403	4.98	5.13
5,000	251.9	386	418	4.85	5.04
6,000	247.6	394	434	4.72	4.96
7,000	243.2	401	451	4.59	4.86
8,000	238.6	407	469	4.44	4.76
9,000	233.8	413	487	4.30	4.67
10,000	228.8	419	506	4.16	4.58
11,000	223.6	424	525	4.01	4.48
12,000	218.3	429	545	3.88	4.39

and liquid are very abnormal, is that the solid is more incompressible than the liquid, although it has a larger volume. It was a matter of great surprise that no other modifications were found. It is almost inconceivable that the liquid should remain permanently of smaller volume than the solid; if we could apply enough pressure we must force the liquid to crystallize into another modification of smaller volume. We must remember, however, that the internal pressure in a metal is already very high, so that we need not be surprised if a very great additional pressure is needed to make it assume another form. It may be mentioned that these experiments show that the effects observed by Ludwig,[41] which he explained by the production of another modification of bismuth under a pressure of 10,000 kgm., must have their explanation in some other direction.

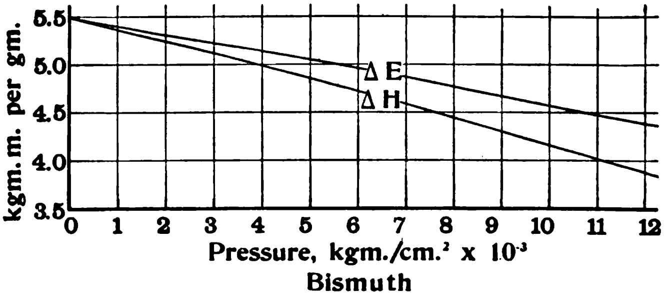

Fig. 19.

Bismuth. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

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[41] A. Ludwig, Jour. Amer. Chem. Soc., Vol. 31, 1130–1136, 1909.

There are several other values for comparison. The melting curves under pressure have been measured by Tammann[38] to 3,000 kgm. and by Johnston and Adams[39] to 2,000 kgm. Tammann gives the melting point at atmospheric pressure as 269.2° and the change of melting temperature with pressure as − 3.9° for 1,000 kgm. Johnston and Adams find for the melting temperature 271.0°, and for the change of melting temperature with pressure − 3.55° for 1,000 kgm. I find by extrapolation 271.0° for the melting point at atmospheric pressure, and for the average slope of the melting curve over the first 2,000 kgm. − 3.60° for 1,000 kgm., agreeing with Johnston and Adams within their limits of error, which they state as 0°.08. Other values of the melting point at atmospheric pressure are: 270.5° on the mercury, and 266.8° on the air thermometer by Person,[42] 271.0° by Vicentini and Omodei[43] on the air thermometer, and 269.2° from an unknown source quoted by Callendar[44] in a table of fixed points. For the change of volume on freezing at atmospheric pressure there are: 0.003 to 0.005 $cm.^3$ per gm. by Nies and Winkelmann,[45] 0.0023 by Roberts and Wrightson[46], 0.003 by Lüdeking,[47] 0.00344 by Vicentini and Omedei,[43] and 0.00336 to 0.00340 by Toepler.[48] In criticism of some of these values it may be said that the bismuth of Nies and Winkelmann was admittedly very impure, the individual observations of Roberts and Wrightson show wide variations, and the bismuth of Lüdeking was known to be impure with a small amount of mercury and its melting point was about 260°. There seems to be only one determination of the latent heat of melting, 12.6 gm. cal. by Person.[42] The value given in the table above is 12.7 cal. The agreement is better than one has a right to expect when one considers the known errors in Person's work, which was performed before modern accurate methods in calorimetry had been introduced.

This completes the list of liquids whose melting curves have been systematically investigated. In addition to these, several others were examined without result for other solid forms, and incidentally some of the melting data were collected. These are now given.

Menthol.—This was from Eimer and Amend, purified by distillation. An attempt to further purify it by crystallization in the thermostat failed; the crystal growth does not take place in the form of large single crystals, but confused aggregates of crystals, in appearance like mould, separate out. The melting point was not carefully determined; it was, however, somewhat higher than 42°, because no trace of melting took place at this temperature in 16 hours in the thermostat. The melting point of the pure substance is given as 42.40° by Hulett,[17] and 42.0° by Bruner.[16] The change of volume on freezing at 77 kgm. was found to be 0.0612 cm.^{3}/gm. The latent heat of menthol is given as 18.9 cal. by Bruner.[16] If we combine my value for ΔV with Hulett's value for $d\tau/dp$, ($= 0.0245$), we obtain for the latent heat 18.5 cal. At room temperature no new modification of the solid was found to 12,000 kgm.; no other temperature was tried. Menthol is known to have an unstable modification, and Hulett has determined its melting curve to 300 kgm. This modification did not appear during the present work.

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[42] C. C. Person, Ann. Phys. et Chim., *76*, 432, 1849.

[43] G. Vicentini and D. Omodei, Atti Torino, *22*, 28–47 and 712–726, 1886–87; *23*, 38–43, 1887–88.

[44] H. L. Callendar, Phil. Mag., Vol. 48, 519–547, 1899.

[45] F. Nies and A. Winkelmann, Wied. Ann., *13*, 43–83, 1881.

[46] W. C. Roberts and J. Wrightson, Brit. Assoc. Rep., 1880, 544.

[47] C. Lüdeking, Wied. Ann., *34*, 21–24, 1888.

[48] M. Toepler, Wied. Ann., *53*, 343–378, 1894.

Anethol.—This was from Eimer and Amend, purified by distillation and by repeated fractional crystallization at room temperature. This was possible because the normal melting point is very close to room temperature. In spite of repeated crystallizations, a substance with sharp freezing was not obtained. The melting point was not carefully determined; it was somewhat over 20°, whereas the melting point of the pure substance is given as 21.3° by Schiff,[22] 21.65° by Landolt,[49] and 22.3° by Block.[18] The change of volume found at 77 kgm. was 0.0793 cm.^{3}/gm. Block gives 0.0794 at atmospheric pressure. Eykmann[20] gives 27.9 cal. for the latent heat. Combining this with a value 0.0800 for the change of volume at atmospheric pressure, gives 0.0194 for $d\tau/dp$. The melting pressure at 100° was found to be in the vicinity of 4,200 kgm. At room temperature there were no new modifications to 12,000 kgm. and none between the melting point and 12,000 at 100°.

Naphthalin.—This was Kahlbaum's purest, redistilled. The melting point was not determined. No new modification was found up to 12,000 kgm. at room temperature or 200°. At 200° the melting pressure is roughly 4,000 kgm. This agrees with the value extrapolated from Tammann's curves. J. Johnston, at the Geophysical Laboratory in Washington, has recently made a careful measurement of the melting curve of this substance (his results are not yet published), so there was no particular object in repeating the measurements here.

Acetophenone.—It was mentioned in the preceding paper[1] that this had not been successfully purified, so that it was not worth while to attempt the determination of the melting curve. The impurity present was sufficient to depress the freezing point from 20.5° to 19.6°. This impurity was not present in sufficient amount, however, to make it seem

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49. H. Landolt, ZS. phys. Chem., *4*, 349–371, 1889.

useless to try if there were other solid modifications. No other forms were found, however, to 12,000 kgm. at room temperature or 200°. At 200° the melting pressure is approximately 11,600 kgm., and the change of volume 0.0454 cm.^{3}/gm.

Antimony Tri-iodide.—This substance was investigated because it is usually listed as showing an enantiotropic transition point at 113°. This is on the authority of Cooke,[50] who is quoted in the Tables of the French Society as stating that the transition is enantiotropic. Cooke really claims two new forms, one with a transition point at 113°, and a rarer one with a point at 125°. Lehmann, however, in his "Molekular Physik," although listing this among substances with enantiotropic modifications, considers that we are not yet sure that the transition is not really monotropic. Furthermore, Groth, in his "Chemische Krystallographie," says that the subject requires further investigation. Groth is of the opinion that Cooke's two forms are monotropic.

The substance used was obtained from Eimer and Amend, and it was not further purified. It contained considerable impurity. No transition under pressure could be found, although unusually careful search was made. At 20° there was none up to 12,000 kgm., and at 150° none from 12,000 down to 600 kgm.; at 90° there was none between atmospheric pressure and 5,500 kgm., and at 120° none between 400 and 8,000 kgm. Furthermore, on heating SbI_3 in the air, no change of color was observed below the melting point. An attempt to make dilatometric measurements was not satisfactory, because the machine oil used as the medium began to attack the SbI_3 at about the supposed transition point with some evolution of gas. However, it was established that there was no large change of volume near 113°.

In the course of the search for the second modification, the melting point at 200.8° was found to be approximately 1,160 kgm., and the change of volume 0.0240 cm.^{3}/gm. The melting point at atmospheric pressure is 163°.

Sodium.—No new measurements were made on this substance, but recently published values by Griffiths[51] for the latent heat of melting at atmospheric pressure allow a very great improvement upon the values listed in the previous paper[1] for the values of ΔH and ΔE at low pressures. Reference is made to pp. 137 and 158 of that paper for the method used in computing the initial value of the specific heat. Broadly speaking, the method was one of compromise between the values indicated by extrapolation from the high pressure measurements, and the direct determinations of other observers. At the time of writing that paper, there was only one determination known of the latent heat, that by Joannis at 13.53 kgm.m./gm. The value indicated by extrapolation from my own work was 12.0, and the compromise value adopted was 12.9. Griffiths' recent value has been determined with great care, and is 11.74, close to the value indicated by extrapolation. The value 11.8 is accepted, therefore, as most probably accurate. This will produce an important change in the values of ΔH and ΔE for the first few thousand kgm., and will remove the initial large and abnormal drop of the curves.

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[50] Cooke, Proc. Amer. Acad., Vol. 13, 174, 1877.

[51] E. Griffiths, Proc. Roy. Soc., Vol. 89, 561–574, 1914.

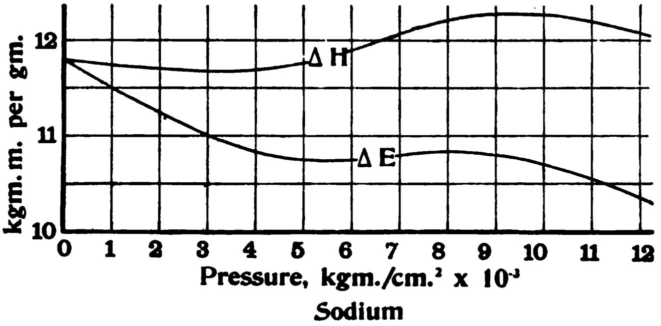

Fig. 20.

Sodium. The latent heat and the change of internal energy when the solid melts to the liquid recomputed from the recent value of Griffiths for the latent heat at atmospheric pressure.

TABLE X.

Sodium [Recomputed Values].

Pressure.	Temperature. °	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	97.62	0.02787	.00860	11.80	11.80
1,000	105.9	2555	816	11.74	11.50
2,000	113.9	2362	778	11.71	11.25
3,000	121.5	2203	744	11.68	11.01
4,000	128.8	2072	712	11.69	10.84
5,000	135.8	1968	684	11.76	10.75
6,000	142.5	1873	654	11.89	10.75
7,000	148.9	1790	626	12.07	10.80
8,000	155.1	1711	600	12.21	10.84
9,000	161.0	1634	578	12.27	10.80
10,000	166.7	1556	558	11.26	10.70
11,000	172.2	1476	540	12.18	10.54
12,000	177.5	1398	522	12.07	10.35

The recomputed curves are shown in Fig. 20, and in Table X. the recomputed numerical values are listed.

It may also be mentioned that the melting point determined by Griffiths, 96.61°, agrees very closely with the two determinations made above, 97.62° and 97.63°. The agreement is closer than that between any other two observers, and 97.62° may, therefore, be accepted as the most probable value.

A remarkable fact discovered by Griffiths is that the specific heat of the liquid at the melting point is less than that of the solid, a result which holds for almost no other substance. See, however, a later discussion for this matter.

(To be concluded.)

THE MAGNETOSTRICTION AND RESISTANCE OF IRON AND NICKEL.

BY C. W. HEAPS.

THE experiments described in this paper were undertaken with the object of making simultaneous measurements of magnetostriction and resistance in the same specimens of iron and of nickel. The importance of making different experiments on the same specimen is very evident when a comparative study is to be made. The galvanomagnetic properties of a metal are so intimately connected with the other properties such as purity, hardness, crystalline structure, etc., that results of different investigators using different samples cannot be compared with each other with any degree of exactness.

The magnetostriction of iron and nickel has been rather extensively studied by different experimenters, and in a general way all results indicate that a bar of iron has its length increased parallel to the direction of a weak magnetic field and decreased when the field is strong. A bar of nickel suffers a decrease in length for all fields. Different samples of these metals, however, behave differently. Bidwell[1] states that he has obtained in one specimen of iron a contraction for all field strengths and S. R. Williams[2] has observed an initial lengthening in the case of nickel. Whether these diversified results are due to differences in the character of the specimen itself or to differences in the uniformity of the magnetic field applied, one can easily see the necessity of making comparative studies from the same sample under the same conditions.

The importance of considering magnetostriction in connection with resistance is made evident by the failure of theory to explain the effect of magnetization upon resistance without bringing into consideration some term depending on the configuration of the molecules in the metal. A magnetic field may cause the free electrons constituting the current to change their paths and hence the resistance is altered. Also, the magnetic field produces a change in the molecular configuration which further affects the resistance. Magnetostriction must also be associated with a change in molecular arrangement, so that by studying magnetostriction one may hope to obtain a clearer insight into the processes of electric conduction.

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[1] Proc. Roy. Soc., Vol. 56, 1894.

[2] PHYS. REV., Vol. 1, p. 257, 1913.

The apparatus used is shown in Fig. 1. The iron or nickel wires, *A* and *A′*, each about 8 centimeters long and .022 centimeter in diameter were contained in a glass tube, *CC′*. By using two wires and a lever, *G*, the effective length of wire was made 16 cm. They were connected as shown so that by joining the copper rods, *K* and *K′*, to a suitable Whaetstone bridge the total resistance of the wire could be accurately measured. Changes of resistance produced by the magnetic field were measured by a method of balancing shunts. Since the resistance of the wires was rather small—less than one ohm—it was necessary to correct carefully for the resistance of the leads. The change of resistance of these copper leads in the magnetic field was neglected. The supporting plugs, *B* and *B′*, were of hard rubber and were firmly cemented into the glass tube. A silk thread extended from the end of *A′* to the lever, *DEF*. One leg of the mirror, *M*, rested on the lever and the other two on a support rigidly attached to the glass tube. The bearings at *G* and *D* were of glass on glass. Each bearing was made by melting down the end of a capillary tube till the hole was nearly closed. Into this depression the fine rounded end of the glass axle was fitted. The image of an electric lamp filament was reflected from *M* upon a scale four or five meters away. Other dimensions were as follows: $FO = 0.2$ cm., $DE = 0.565$ cm., $EF = 3.0$ cm. The magnifying power was calculated to be 32,890. In order to be sure that no disturbing effects were present the wires, *A* and *A′*, were replaced by silk threads and the apparatus placed in the magnetic field. No deflection resulted when the magnetic field was thrown on or off. Throughout the experiment the weight *W* was 40 grams and the temperature was that of the room—about 22° C.

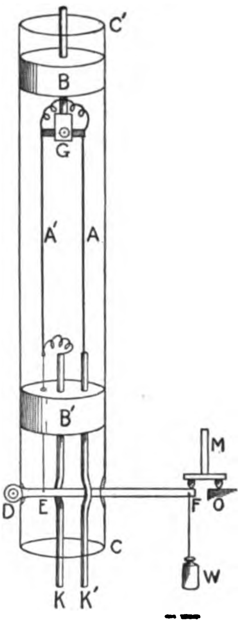

Fig. 1.

The longitudinal magnetic field was furnished by a solenoid 15 cm. long and giving a field of 100 C.G.S. units for a current of one ampere. No attempt was made to correct for the non-uniformity of the field, though this non-uniformity might be quite a factor in the case of such a short solenoid. However, as the resistance and the magnetostriction could be measured without moving the apparatus, any irregularity in the field would probably not affect the value of the data as far as purposes of comparison are concerned.

For producing the transverse field a Weiss electromagnet with pole-pieces 10 cm. in diameter was used. The glass tube of the apparatus was made to have a small diameter so that the pole-pieces could be brought as close together as 1.7 cm. Of course inaccuracy in adjusting the apparatus would introduce a small longitudinal component of magnetization. Jones and Malam[1] have shown that an error of one degree in adjusting the apparatus may affect the results obtained to a slight extent. However, such small errors in the present experiment would not affect comparative study. The magnetic field was measured by the use of a bismuth spiral. The chemical composition of the metals was not definitely determined. Soft Norway iron wire was used in one case. The nickel was of the ordinary kind furnished by Eimer and Amend.

In taking the data it was found inadvisable to make simultaneous observations of resistance change and length change, because the current through the wire produced disturbing heat effects. Consequently a series of readings for magnetostriction was taken and immediately afterwards a series for resistance. Hysteresis effects were not studied, the observations beginning in every case with a maximum field and ending with the weak field. In the case of nickel the specimen was moved and readjusted between the series of observations, but the accuracy of readjustment was such that any error introduced would be very slight. When iron was used care was taken not to touch the apparatus between observations.

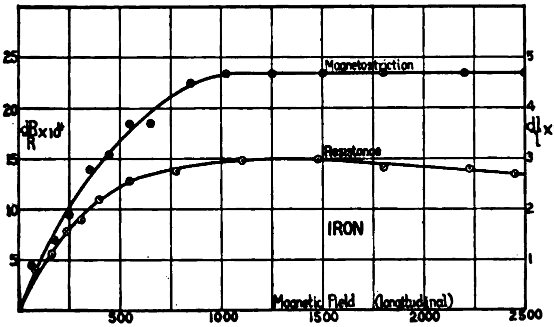

Fig. 2.

The curves shown are plotted from the data obtained, dl/l being change of length divided by length, and dR/R change of resistance divided by resistance. The external magnetic field measured in gauss is plotted without correction being made for the demagnetizing effect of the metal wires. If the resistance increased, values of dR/R are plotted above the axis of abscissæ; while if the length decreased dl/l is plotted above the axis on the same diagram except in Fig. 5, where dl/l reprseents a contraction. The resistance curves are similar in every respect to the ones previously obtained by the writer.[1]

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[1] Phil. Mag., Vol. 27, 1914, p. 649.

The drop in the resistance curve of Fig. 2 is due to transverse magnetization. It has been shown[2] that with the pure metal and uniform fields there is no initial increase of resistance in a transverse field for either iron or nickel. It is as yet difficult to say whether impurities or a longitudinal component of magnetization is responsible for the initial increase observed in iron in the present experiments.

The magnetostriction curves differ in some respects from the majority of the published results. Iron was found to contract for all values of the longitudinal magnetic field. This contraction is in agreement with one of Bidwell's curves but is at variance with the results of other workers. The transverse field also produced a contraction, though it is possible that in larger fields an elongation might result, as the course of the curve indicates that "saturation" has not been reached at 12,000. In nickel the transverse field produced an elongation and the longitudinal field a contraction.

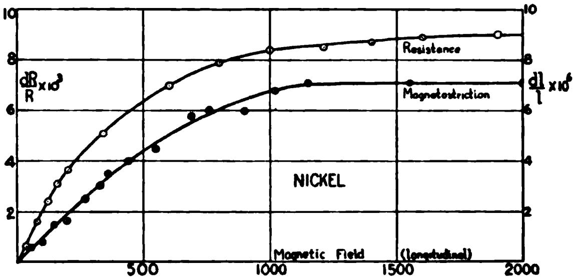

Fig. 3.

In Figs. 2 and 3 there is remarkable parallelism between the resistance curves and the magnetostriction curves. An increase of resistance is associated with a decrease of length, and it seems probable that whatever causes operate to change the resistance also operate according to much the same law to change the length of the conductor. According to Drude's theory of metallic conduction the electric current is given by

$$I = \frac{1}{2} N \frac{e^2}{m} X \frac{L}{u},$$

where N is the number of electrons per unit volume, X is the electric force, u the average velocity of the electrons, and L the mean free path.

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[1] Phil. Mag., Dec., 1911, p. 900.

[2] Jones and Malam, l. c. R. A. Heising, Phys. Rev., Vol. IV., 4, 1914, p. 315.

This equation is usually assumed to hold true even in the newer theories of metallic conduction, where application of the quantum hypothesis is made. Presumably, by changing the arrangement of the molecules, the longitudinal magnetic field affects L. If L is made smaller the resistance is increased. Let I' be the current when the magnetic field acts. Then

$$I' = \frac{1}{2} N \frac{e^2}{m} X \frac{L'}{u} = \frac{X}{R'},$$

where L' is the new free path and R' the new resistance. Subtracting this equation from the first gives

$$\frac{1}{R} - \frac{1}{R'} = \frac{1}{2} \frac{Ne^2}{mu} (L - L')$$

or

$$\frac{dR}{R} = \frac{dL}{L}.$$

Here dL is the decrease in L while dR is the increase in R. It seems reasonable to suppose that when the intermolecular distances are made smaller the length of the conductor as a whole should decrease proportionally. That is, we might expect

$$\frac{dL}{L} = C \frac{dl}{l},$$

where C is a constant and l is the length of the conductor. Hence,

$$\frac{dR}{R} = C \frac{dl}{l}.$$

In Fig. 6 the values of dR/R are plotted against corresponding values of dl/l. In the case of iron a straight line results as is to be expected from the above theoretical considerations. No values are taken from the resistance curve for fields above 1,200, as transverse magnetization causes a drop above that point. The curve of Fig. 6 for nickel is also a straight line for large fields but for small fields the law of direct proportionality no longer holds. W. A. Jenkins[1] has studied magnetostriction and resistance in different specimens of nickel and he comes to the conclusion that dR/R is proportional to $\sqrt{dl/l}$ for fields below 100 C.G.S. units. For larger fields than this the law will not hold. Data taken from the observations of other experimenters do not support Jenkins' conclusion, though, as was pointed out above, data obtained from different samples may give different results. The crystalline structure of a nickel rod may be quite different from that of a drawn wire. However it seems possible that in the case of nickel one cannot assume the change of intermolecular distance for small magnetic fields to be proportional to the total change of length as in iron.

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[1] Phil. Mag., Vol. 27, 1914, p. 731.

In the case of a transverse magnetic field two factors enter to change the resistance—(1) the molecular rearrangement, and (2) the direct deflection of the electrons by the magnetic field.[1] We would therefore expect the magnetostriction and resistance curves of Figs. 4 and 5 to resemble each other only when term (1) is large compared with term (2). This seems to be the case in the nickel specimen studied, though even here the effect of term (2) is evident. When the magnetic field is made as large as 6,000 the molecular rearrangement is complete and the length ceases to increase. The resistance, however, continues to decrease slightly as the field increases, and this decrease must be attributed to the magnetic deflection of the electrons.

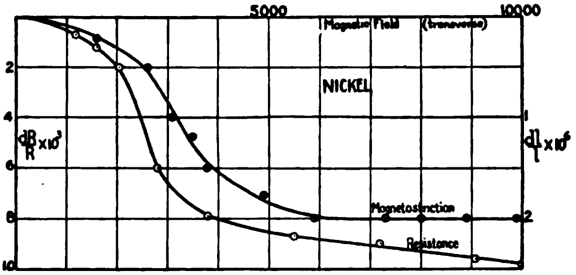

Fig. 4.

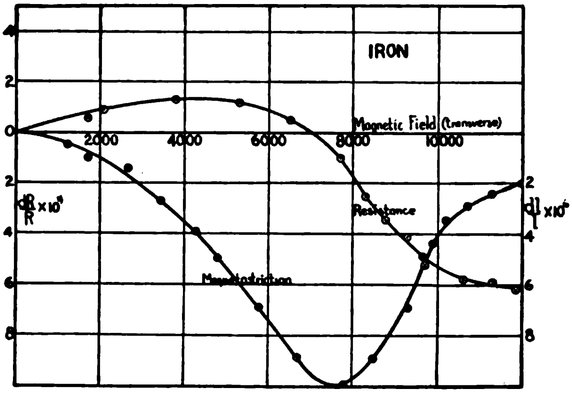

Fig. 5.

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[1] For a longitudinal field (2) also produces an effect, but it is smaller than for a transverse field. The writer has calculated the magnitude of (2) to be $\frac{1}{36} H^2 \frac{e^2}{m} T^2$ for a longitudinal field. For a transverse field it is $\frac{1}{4} H^2 \frac{e^2}{m} T^2$. (E. P. Adams, Phys. Rev., May, 1907, p. 428.)

The curves for iron (Fig. 5) show that the molecular rearrangement is not complete for fields as large as 12,000. That is, the length change is still dependent on the magnetic field when it has that value. This would seem rather surprising were it not probable that the intensity of magnetization and not the magnetic field is the factor which determines the form of the curves, and it is much more difficult to magnetize wires transversely than longitudinally. The complex nature of the magnetostriction curve for iron would lead one to expect a complex resistance curve, such as is shown, especially if the two factors mentioned above as determining the resistance change are simultaneously operative. It is perhaps significant that as long as a transverse magnetic field produces an increase in the resistance of iron the contraction of the iron increases. When the resistance change becomes negative the contraction begins to decrease in magnitude.

In all of the curves except those of Fig. 5 the resistance increase is coupled with a length decrease, and vice versa, and for iron the tendency is towards this relation as is pointed out above. Guthe and Austin[1] have found an increase in the length of Heusler alloy placed in a magnetic field. The previous experiments[2] of the writer on this metal have shown that the resistance decreases, and the curve obtained is similar to the magnetostriction curves of Guthe and Austin. Though a law of direct proportionality may not hold good in all cases it is noteworthy that those metals showing large magnetostriction also show a large resistance change. The magnitude of the two effects follows the order: nickel, Heusler alloy, iron. If the analogy holds good for other metals we might expect dl/l in the non-magnetic metals to be of the order 10^{-8} or 10^{-9}.

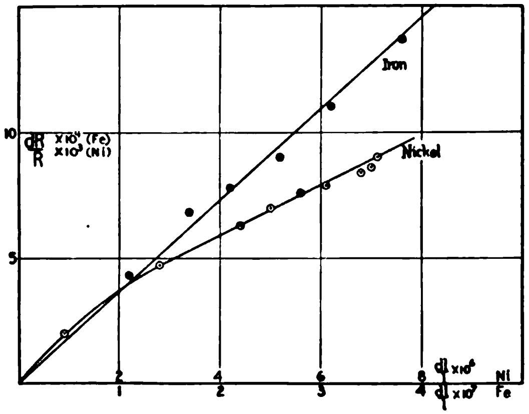

Fig. 6.

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[1] Bull. Bur. Standards, 2, 297, 1906.

[2] Phil. Mag. Dec., 1911, p. 900.

The substitution of experimental data in any of the formulæ derived from our present theories of electric conduction cannot carry one very far on the road towards proving these theories. The mathematical expression for the resistance change in a transverse field is

$$\frac{dR}{R} = \frac{dT}{T} - \frac{1}{4}H^2\frac{e^2}{m}T^2,^{1}$$

where T is the free period of the electrons in the metal. Various attempts have been made to explain experimental results using this equation—Jenkins finding it unsatisfactory and Jones and Malam meeting with fair success. It is doubtful whether sufficient data can be obtained to justify numerical substitutions in the above equation since H cannot properly be taken as the external magnetic field or the magnetic induction. It is more proper to consider it as corresponding to the "molecular field" of Weiss's magnetic theory, and the changes produced in this molecular field by an external field must be of a very complex character.

The data obtained in this experiment permit of a comparison being made between the longitudinal and transverse magnetostrictive effects, though as has been pointed out by S. R. Williams, the crystalline structure parallel to the length of a wire is different from that perpendicular to the length, so that comparisons cannot be carried too far. If we neglect this factor we find that iron contracts at right angles to the magnetic field as well as parallel to the field. The resulting decrease of volume per unit volume is of the order 10^{-6}. Nickel expands perpendicularly to the field and contracts in the direction of the field. The calculated maximum decrease in volume of nickel is 3×10^{-6}. These conclusions are in contradiction to the experiments of Nagaoka and Honda who found an increase in volume for both iron and nickel.

S. R. Williams, in a series of recent articles, has sought to attribute magnetostriction to the orientation of molecular magnets having the form of oblate spheroids. For this theory to hold good transverse elongation of a conductor would have to be associated with longitudinal contraction, and vice versa. In nickel this is the case, but in iron the phenomena seem to be of too complex a nature to allow of such a simple explanation. It is probable that some sort of structural modification takes place in which the molecular grouping is changed by the magnetic field, and this changed molecular grouping may be taken in connection with a theory of oblate spheroids to explain most of the phenomena observed.

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[1] E. P. Adams, Phys. Rev., May, 1907, p. 428.

SUMMARY.

1. The specimen of iron was found to contract when magnetized either transversely or longitudinally.

2. The specimen of nickel contracts in the direction of a magnetic field and expands perpendicularly to the magnetic field.

3. For a longitudinal field the magnetostriction and resistance curves are found to be very similar—in iron the resistance increase is proportional to the contraction.

4. For a transverse field the magnetostriction and resistance curves of nickel are very similar, showing a close relationship between the two effects. In iron the relationship is also evident, but is more complex than in the case of nickel. A decrease of resistance is associated with a diminution of magnetostriction, and an increase of resistance with an increase of magnetostriction.

5. Except with iron in a transverse field contraction is always coupled with an increase of resistance and expansion with a decrease of resistance.

6. Application of the electron theory to the experimental results is as satisfactory as could be expected, though ignorance of the laws governing intermolecular actions in different metals prevents to a considerable extent the testing out of any theory.

THE RICE INSTITUTE,
HOUSTON, TEXAS.

A MODIFIED VARIABLE CONDENSER FOR USE WITH THE QUADRANT ELECTROMETER.

By Harry Clark.

In the use of the quadrant electrometer to measure very small currents the best results are obtained by the use of a compensation method, that is, one in which the current to be measured is neutralized by an equal current of opposite sign produced in such a way that its value may be calculated. Thus the electrometer is used only as a detecting instrument and its quadrants remains always at zero potential.

Such a current may easily be produced either by the use of a quartz piezo-éléctrique or by a condenser, one terminal of which is connected to the electrometer while the potential of the other is regulated in any convenient way. The *standard condenser method* consists in varying this potential between known limits while the capacity is kept constant. In the *variable condenser method* the potential remains fixed while the capacity is varied. By any of these methods a known quantity q of electricity is delivered to the electrometer at any desired rate, and the average value of the current is given by q/t where t is the interval of time during which compensation is effected.

Ideally the procedure in making a measurement might be as follows: The unknown steady current is deflected into the insulated quadrants of the electrometer, and at the same instant the chronometer is started and compensation is begun. The spot of light is held at zero by careful manipulation of the compensating apparatus until the whole charge q (depending on the limitations of the particular apparatus used) has been delivered, at which instant the chronometer is stopped.

It is difficult for the operator whose attention is fixed on the spot of light to anticipate this latter instant. He must therefore stop the chronometer without warning. Since it is also difficult to keep the needle exactly on zero, he cannot be sure that the quadrants were at zero potential precisely at that instant.

In practice much better results are obtained with less fatigue to the observer by adopting the following slightly varied procedure: the current to be measured is deflected into the electrometer and the spot of light is allowed to depart from its zero position. As it passes some convenient point, say the one-centimeter mark, the chronometer is started. Compensation is then begun, and the spot of light is brought back to zero and held there as nearly as may be until the entire compensating charge has been delivered. The spot of light again departs from zero, and as it passes the one-centimeter mark the chronometer is stopped. Slight irregularities in the movements of the needle, due to faulty manipulation, are thus partly damped out, and the instants of starting and stopping the chronometer are sharply defined. If measurements made in this way are to be accurate, both the starting and stopping of the chronometer must be retarded by the same amount, which will be true only in case the capacity of the apparatus has the same value at the end of the experiment as at the beginning. While this requirement is fulfilled by both the quartz piezo-éléctrique and the standard condenser, it is obviously unsatisfied by the ordinary variable condenser.

The method to be described overcomes this difficulty completely. It consists essentially in the use of two variable condensers. One terminal of each condenser is connected to the insulated quadrants of the electrometer, the other terminals being maintained at potentials *V* and zero respectively. The entire compensation current is produced by varying the capacity of the first condenser. If the second is varied at such a rate that the sum of the two capacities remains constant the sensitivity of the apparatus will not be changed.

As used by the writer these two condensers are combined into a single instrument indicated in Fig. 1. The fixed plates at *A* serve as a common electrode for both capacities and communicate with the electrometer, *D*, and the source, *G*, of the unknown current. The movable piles of semicircular plates, *B* and *C*, though rigidly mounted on the same support and constrained to rotate together, are insulated from each other. *B* is kept at any desired potential by means of a battery *F*, while *C* is put to earth.

Some of the details of the apparatus may be seen in Figs. 2, 3, 4, and 5 which are about one fifth actual size. The pile of fixed plates shown at the right in Fig. 5 consists of two pairs separately supported and insulated with amber. By means of the platinum-tipped screw seen at the left in Figs. 2 and 4 it is possible to connect one or both pairs to the electrometer, thereby greatly increasing the range of usefulness of the instrument. The movable piles communicate with the battery and earth respectively through small spiral springs shown in Fig. 3. All metal parts save the central steel shaft which is completely enclosed are made of the same metal, brass, to reduce the Volta effect, and the trouble from accidental charges on insulators is reduced to a minimum by screening.

PHYSICAL REVIEW, VOL. VI., SECOND SERIES.
July, 1915.

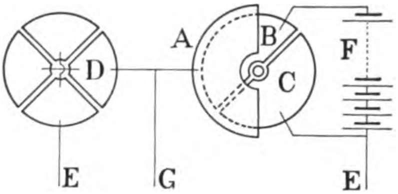

Fig. 1.

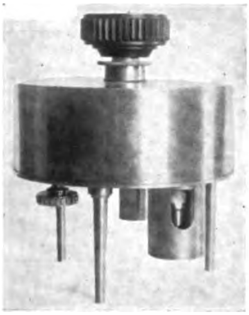

Fig. 2.

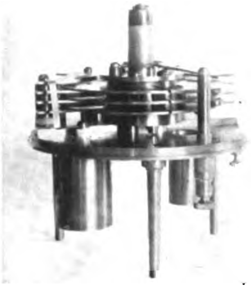

Fig. 3.

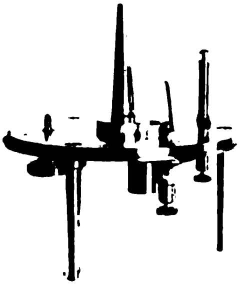

Fig. 4.

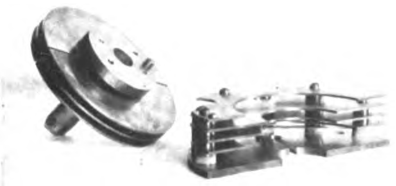

Fig. 5.

HARRY CLARK.

The advantages of this modified variable condenser method are obvious. By comparison with the quartz piezo-éléctrique the apparatus is cheaper, less fragile, better insulated and less sensitive to moisture, has any desired range of values, and is much more easily manipulated and less fatiguing to the operator especially in measurements of long duration. The standard condenser method requires a potentiometer operating continuously or nearly so over a wide range of voltage and such instruments usually consume an appreciable current and are difficult to use. The variable condenser uses so little current of course that very small cells may be employed, small cadmium cell for example. The apparatus described in this paper has been used by the writer and has been found to operate consistently with no appreciable error, certainly better than two parts in a thousand.

The writer desires to extend thanks to M. Jacques Danne of Gif, S-et-O, France, in whose laboratory the idea of the modified condenser was partly worked out.

Jefferson Physical Laboratory,
Cambridge, Mass.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

WASHINGTON MEETING, APRIL 23 AND 24, 1915.

MINUTES OF THE SEVENTY-SEVENTH MEETING.

A REGULAR meeting of the American Physical Society was held at the National Bureau of Standards, Washington, on Friday and Saturday, April 23 and 24, 1915.

Friday, 2:00 P.M.

Hon. William C. Redfield, Secretary of Commerce, opened the meeting with a cordial address of welcome in which he gave strong expression to his interest in the progress of science, and his belief in the vital interdependence of physics and the commercial interests of the country.

Papers were presented as follows:

On the Distributed Capacity of Single Layer Solenoids. (By title.) J. C. HUBBARD.

The Skin Effect in Bimetallic Wires. JOHN M. MILLER.

Magnetization by Rotation. S. J. BARNETT.

Intercomparisons of the Standard Instruments at Magnetic Observatories, 1905–1914. L. A. BAUER.

Simultaneous Readings in Electrical Measurements, with Demonstration of a New Type of Switch for Facilitating Them. WALTER P. WHITE.

The General Design of Critically Damped Galvanometers. (By title.) FRANK WENNER.

Apparatus for the Simultaneous Measurement of Length, Electrical Resistance, and Magnetic Permeability as Functions of the Temperature. (By title.) ARTHUR W. GRAY.

The Dielectric Constant of a Heterogeneous Dielectric. H. L. CURTIS AND M. JAMES.

The Separately Excited Electrodynamometer as a Sensitive Galvanometer. ERNEST WEIBEL.

The Crushing of a Hollow Conductor by Lightning. (By title.) W. J. HUMPHREYS.

Aneroid Barometers. M. D. HERSEY.

A Method of Measuring Heat Conductivities. R. W. KING.

Viscosity of Ethyl Ether near the Critical Temperature. A. L. CLARK.

An Equation of State for Normal Substances, Tested in the Vapor Dome. HARVEY N. DAVIS.

The Correction of Echoes in the Auditorium at the University of Illinois. (By title.) F. R. WATSON.

The Transpiration of Plants in relation to Temperature and Solar Radiation. LYMAN J. BRIGGS AND H. L. SHANTZ.

A Mercurial Barometer in which the Well Setting is Eliminated. LYMAN J. BRIGGS.

Saturday, 9:30 A.M.

The Reflecting Power of Metals for the Ultra-Violet Region of the Spectrum. EDWARD O. HULBURT.

The Visibility of Radiation in the Red End of the Visible Spectrum. EDWARD P. HYDE AND W. E. FORSYTHE.

The Effective Wave-Length of Transmission of Red Pyrometer Glasses and Other Notes on Optical Pyrometry. EDWARD P. HYDE, F. E. CADY AND W. E. FORSYTHE.

The Use of a Hollow Filament with Perforations in the Determination of the Black-body-Temperature and True-Temperature Relation for Tungsten. A. G. WORTHING.

A Further Extension of the Spectrum in the Extreme Ultra-Violet. THEODORE LYMAN.

The Fluorescence and Absorption Spectra of Uranyl Nitrate. E. L. NICHOLS AND ERNEST MERRITT.

A Precision Artificial Eye. (By title.) HERBERT E. IVES.

A Flicker Photometer Attachment for a Lummer-Brodhun Photometer Head. E. F. KINGSBURY.

Color Grading and Color Specifications by Means of the Rotary Dispersion of Quartz. (By title.) IRWIN G. PRIEST AND CHAUNCEY G. PETERS.

A Proposed Method for the Photometry of Lights of Different Colors. IRWIN G. PRIEST.

On X-Ray Wave-Lengths. WILLIAM DUANE AND F. L. HUNT.

The X-Ray Spectrum of Tungsten at a Constant Potential. DAVID L. WEBSTER.

Factors Governing the Darkening of a Photographic Plate by X-Rays. J. S. SHEARER.

The Wave-Length Sensibility Curve for Isolated Crystals of Selenium between 200 $\mu\mu$ and 450 $\mu\mu$. L. P. SIEG AND F. C. BROWN.

The Variation of Equilibrium Conductivity of Selenium with the Intensity of Illumination. F. C. BROWN.

The Effect of Variation of Temperature on the Coefficient of Recombination of Electrons in a Selenium Crystal. KATHRYN J. DIETERICH.

Saturday, 2:00 P.M.

A Null Method with Photo-Electric Cells. F. K. RICHTMYER.

New Tests of Einstein's Photo-Electric Equation. R. A. MILLIKAN.

Factors Affecting the Relation between Illumination and Photo-electric Current. HERBERT E. IVES, SAUL DUSHMAN, AND E. KARRER.

The Theory of Adsorption. IRVING LANGMUIR.

The Law of Stokes and the Removal of Particles from Fluids. W. W. STRONG.

Ionization Potential of an X-Ray Tube. E. C. DREW. (Introduced by HORACE C. RICHARDS.)

Parson's Magneton Theory of Atomic Structure. DAVID L. WEBSTER.

A Conducting Paint. M. JAMES.

Mechanical Strain and Thermo-electric Power. WALTER P. WHITE.

Recent Results and Conclusions Regarding Specific Heats at Moderate and High Temperatures. (By title.) WALTER P. WHITE.

Geometrical Tripods and Stands. LYMAN J. BRIGGS.

Changes in Electrical Resistance Accompanying Thermal Expansion, ARTHUR W. GRAY.

The Ballistic Use of a Moving Coil Galvanometer in Measuring Discharges Obeying the Exponential Decay Law. A. G. WORTHING.

The Mobilities of Ions in Air. E. M. WELLISCH.

The Effect of a Magnetic Field on the Initial Recombination of the Ions Produced by X-Rays. (By title.) J. E. M. JAUNCEY.

An Accurate Method for the Measurement of the Conductivity of Electrolytes. (By title.) W. A. TAYLOR AND H. L. CURTIS.

The thanks of the Society were extended to the Washington members for the luncheon generously provided on Saturday for all visiting physicists and to the Bureau of Standards for numerous courtesies extended.

On Friday evening a large number of the members in attendance dined together at the Cosmos Club. This pleasant feature was arranged for and carried out by Dr. L. J. Briggs, of the Bureau of Plant Industry.

The attendance at all sessions was good, and there was considerable profitable discussion of papers. On account of the length of the program, a number of local members courteously yielded their time to others and presented their papers by title only.

A. D. COLE,
Secretary.

Note on the Construction of a Short Vacuum Gauge.[1]

By E. Karrer.

THE gauge herein described is in general form and manner of working exactly like the Gaede gauge. Its construction, however, is simpler and very much more durable, due to the entire elimination of rubber tubing.

The Gaede[2] gauge referred to is well known as an improved McLeod gauge. In the Gaede gauge the mercury reservoir is closed air-tight, so that the mercury column need not be of barometer height, but may be very short.

The reservoir of the Gaede gauge is, as in the McLeod gauge, connected to the compressing chamber by means of rubber tubing. In order to keep this connecting rubber tubing sufficiently flexible and air-tight it is enclosed in another rubber tube which is exhausted.

In the gauge shown in the figure below the mercury reservoir (*lm*) is directly connected to the gas chamber by means of glass tubing. (*cd*) is a capillary tube to facilitate reading the height of the mercury in (*ab*) accurately. (*cd*) and (*ef*) are of the same bore to avoid error due to capillarity. The dimensions of the gauge are as follows:

(*ab*) 23.3 cm. long.
(*cd*) capillary, 1.5 mm. bore, 4.5 cm. long.
(*ef*) capillary, 1.5 mm. bore, 11.5 cm. long.
(*ef*) capillary, 1.5 mm. bore, 11.5 cm. long.
(*gh*) 2 cm.; (*hi*) 7.3 cm. long; (*ik*) 13 cm.; (*kl*) 25 cm.; (*ko*) 41 cm.
Bulb (*fg*) 2.8 cm. diameter.
Bulb (*lm*) 3.2 cm.
Manometer (*vw*) 11.5 cm. long.
(*tu*) is guide for (*ko*), made of 1.5 × 2.3 cm. wood strips.
(*ko*) is made of glass tubing, 1.4 cm. diameter with walls 1.2 mm. thick.
All other parts are made of glass tubing 0.9 cm. diameter, with walls 0.8 mm. thick.

(*i*) is a ground-glass joint, so called "normal," made by Leybold's Nachfolger, Germany.

(*rs*) is wood bearing for the movable tube (*ko*), with spring (*pq*) to keep the ground-joint (*i*) together.

The tube (*ko*) forms with (*ik*) a "T," the end of (*ik*) being ground to fit the end of (*ij*), also ground. The end of (*jk*) is closed and fits in a depression in a brass spring (*pq*) which keeps the ground joint (*j*) together.

To make a determination of pressure the reservoir (*ko*) is raised, rotating about the ground joint as axis, until the mercury stands at a fixed height in (*cd*). The mercury in (*ef*) will stand at a height, depending upon the pressure of the gases which are compressed into it.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 31, 1914.

[2] Dr. Anderson, of Baltimore, has pointed out to me that the McLeod gauge may be made to indicate negative pressures. Possibly this is the same phenomenon.

Alongside of (*ef*) is a scale giving the pressure of the gas in the system at the time the gas was compressed into the capillary corresponding to any height of the mercury in (*ef*). This scale gives pressures from 1 mm. to 0.0001. This lower limit was conditioned only by the capillary tube (*ef*) and its bulb, which were taken from the Gaede gauge. The bulb has a capacity of 15 c.c. Gaede gauges may be obtained with a lower limit of .00001. Only certain scale divisions are shown in the figure.

The pressures indicated by the scale are obtained from Boyle's law, after the volume of all portions of the capillary along its full length and the volume of the chamber (*gh*) have been determined. An auxiliary gauge (*vw*) indicates pressures from 100 mm. to 1 mm.

The mercury should always be halted while rising in the capillary tubes, otherwise the mercury in capillary (*ef*) may stand at a higher level and as a consequence indicate pressures much too low.[1] Errors resulting from this cause may be considerable at low pressures. Possibly the cleanliness of the glass surface has something to do with this phenomenon of the lagging of the mercury in the capillary. Tapping the capillary slightly causes the mercury to fall back in such cases.

In filling the gauge with mercury care must be taken to free the mercury reservoir from air as completely as possible by heating the tube. There are several methods that may be followed in filling. Possibly some method as described by Kahlbaum[2] in filling the ordinary McLeod gauge might be followed.

The method used to fill the new short gauge described here was the following: On the end of mercury tube (*ko*) was sealed a stopcock to whose further end was sealed a short tube of large bore. After thorough drying of the tube (*ko*) the cock is opened and the mercury poured in. The stopcock is then closed and the air exhausted while the mercury is heated along its whole length. Whatever air collects at the upper end of (*ko*) near the stopcock may later be forced out by lowering the mercury column with stopcock open. When the mercury has been freed from air, the tube (*ko*) is raised slightly and the gauge exhausted until the mercury falls some convenient distance below the stricture that had previously been made in the bore. At this stricture the stopcock is sealed off. The amount of mercury necessary is less than .5 kg.

The tube (*ko*) might be made of thick-walled tubing of smaller bore, necessitating a much smaller amount of mercury.

A simpler method of filling perhaps would be to disconnect the gauge from the pump entirely and fill like the ordinary mercury manometer by heating and tilting. In this case the end of (*ko*) is sealed beforehand and the bulb may be placed at the extreme end. With this manner of construction the gauge may be made much smaller and lighter, so that it may be more directly attached to the space that is evacuated.

By varying the constricted portion of the tube between the gas volume bulb and the ground joint the gauge may be made to act as slowly as desired. When this passage is too large the mercury reservoir must be raised cautiously; otherwise the mercury as it reaches the top of the bulb may splash up into the capillary.

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[1] Described in circulars of makers, Leybold's Nachfolger, Germany.

[2] Ztschr. f. Instrumentedkunde, XV., p. 192 (1895).

The gauge is entirely free from the annoyances caused by the use of rubber tubing. The mercury is not contaminated by abrasion of the rubber tubing and no leaks will ordinarily develop merely with age, as in any rubber parts.

The tube (*ko*) moves between two guides (*tu*), so that no undue strain is put on the ground joint during manipulation. The guides also afford a convenient support for the hand during the raising of the mercury reservoir.

The chief advantages of the gauge as described in this paper, in addition to those that the Gaede construction affords, viz: large range, sensitiveness, direct reading, small size, accuracy and quickness, are simplcitiy, durability and assurance that no portion is liable to disintegrate under ordinary laboratory conditions as rubber parts do.

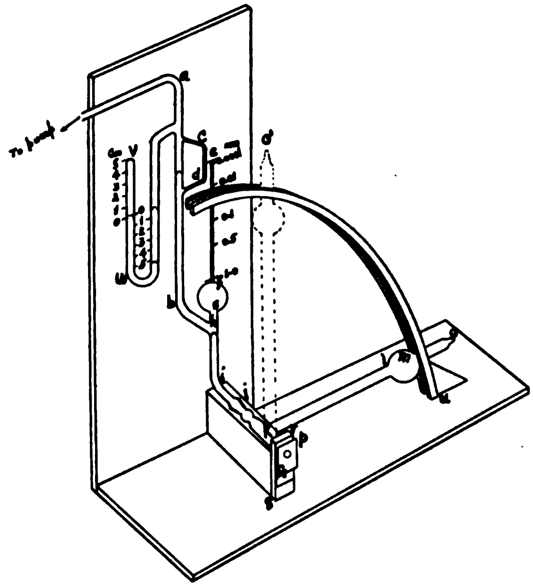

Fig. 1.

After the gauge had been constructed and this description written my attention was called to an improved gauge recently described by Reiff.[1]

The gauge described by Reiff is ingeniously designed to eliminate all rubber tubing. However, it is not so simple as the gauge herein described. The article referred to contains an excellent sketch of the development of the McLeod gauge.

Reference is also made to a gauge designed by Rheden,[2] probably very similar to the form of gauge described here. The German patent files in which this is described were not accessible however.

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[1] Zeitschr. Instkde., April, 1914, pp. 96–106.

[2] U. Rheden, D. R. G. M., 404499.

I wish to express my appreciation of the keen interest taken by Dr. H. E. Ives in this work.

Gauges of the design described above are constructed by Ruckstahl and Luchs, Wilkinsburg, Pa.

PHYSICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY,
PHILADELPHIA, PA.

ELECTRIC FURNACE EVIDENCE ON THE RELATION OF SPECTRUM LINES HAVING CONSTANT DIFFERENCES IN WAVE-NUMBER.[1]

BY ARTHUR S. KING.

PAIRS of lines occur in many spectra for which the differences between the reciprocals of the wave-lengths is very nearly the same for a number of different pairs. These regularities suggest some sort of series relations among the lines, and a comparison of the behavior of the members of such pairs under different physical conditions is of interest in this regard.

Paulson has recently picked out a large number of these pairs of lines, and many of them in the spectra of iron, titanium, and vanadium have been classified by the writer according to their behavior in the electric furnace at different temperatures. In the majority of cases, the members of a pair are in the same furnace class, but the number of exceptions is large enough to be significant. A number of pairs occur for which the component lines are separated by more than one class in the furnace classification. This is greater than the uncertainty involved in the assignment to classes and renders it improbable that both lines in such pairs can be emitted by the same vibrating center. The evidence thus supports the view that these pairs are by-products of series relations, rather than that the lines of the pairs are members of the same undiscovered series.

MOUNT WILSON SOLAR OBSERVATORY,
December 10, 1914.

THE BALLISTIC USE OF A MOVING-COIL GALVANOMETER IN MEASURING DISCHARGES OBEYING THE EXPONENTIAL DECAY LAW.[1]

BY A. G. WORTHING.

FOR the purposes of the present paper, a discharge obeying the exponential decay law has been defined as that discharge which occurs when there is an intrinsic E.M.F. of the exponential decay type in the circuit. Close approximations to such discharges are quite common. Due to the distorting effect of the counter E.M.F. resulting from the generator action of a moving coil or a moving needle, the simpler type in which the current obeys a similar law will be rarely met with in practice.

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 29–31, 1914.

Neglecting the self-induction of the galvanometer circuit—the error in practical cases is usually negligible—the equation giving the ratio of the deflection for an impulsive discharge to the deflection for a prolonged discharge of the same quantity according to the exponential decay law in a so-called radial field, is

$$\phi = \frac{T'}{T} \frac{e^{-2\lambda' \frac{\tau'}{T'}}}{e^{-2\lambda \frac{\tau}{T}}} \frac{\sin 2\pi \frac{\tau'}{T'}}{\sin 2\pi \frac{\tau}{T}},$$

where ϕ is the ratio sought, λ, T and τ the logarithmic decrement, the period and the time required for the coil starting at rest to reach its maximum deflection for the case of the prolonged discharge, and λ', T' and τ' the corresponding terms for the case of the impulsive discharge. Theoretical expressions for τ and τ' in terms of the galvanometer constants and of the time-constant of the discharge enable one to obtain the factor ϕ' from easily obtainable data.

For a particular experimental case where $T = T' = 7.35$ sec., where $\lambda = \lambda' = 0.692$ and where the time-constant of the discharge was 1.06 sec., ϕ was found to be 1.296.

By varying the moment of inertia of the galvanometer coil and the resistance in its circuit, several periods varying from 4.3 sec. to 21.5 sec. were obtained in this test. With one exception the computed values for ϕ were found to agree exceedingly well with the observed values.

In case a certain discharge is known to obey the exponential decay law, its time-constant may be determined from observation of the throws obtained with the characteristics of the galvanometer varied as indicated above. That time-constant which leads to a set of values for ϕ which are consistent with the observed throws is the one sought.

This method of obtaining a time-constant has been used with considerable advantage in accuracy in a modification of a method of measuring thermal capacities at incandescent temperatures, given by Corbino, an application of whose method, in attempting to verify certain results reported in November, 1914, led in fact to the present paper.

Nela Research Laboratory,
National Lamp Works of General Electric Co.,
Nela Park, Cleveland, Ohio.

The Mobilities of Ions in Air.[1]

By E. M. Wellisch.

THE mobilities of the positive and negative ions formed in thoroughly dried air by the alpha rays of polonium were determined over a wide range of pressures. In the case of the negative ion the results were normal from a pressure of 1 atmosphere down to about 8 cm.; below 8 cm. the negative carriers were found to consist of two kinds, electrons and ions, the former increasing in number relatively to the latter with diminishing pressure. No evidence was found of an intermediate or transition stage, the separation between the faster and the more slowly moving carriers remaining throughout well defined. The mobility of the negative ion was found to vary inversely as the pressure down to the lowest pressure employed ($\frac{1}{7}$ mm.); this indicates that the negative ion remains unaltered in nature over this wide range of pressures.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

The positive ion was found to remain unchanged from 1 atmosphere down to $\frac{1}{20}$ mm. which was the lowest pressure tried.

SLOANE LABORATORY,
YALE UNIVERSITY,
April 12, 1915.

PARSON'S MAGNETON THEORY OF ATOMIC STRUCTURE.[1]

BY DAVID L. WEBSTER.

IN a previous paper[2] the author has shown that by means of Parson's concept of the magneton one may eliminate certain serious conflicts of Planck's theory of heat radiation with the phenomena of refraction and related optical effects, and still keep the essential features of Planck's argument. The present paper gives an account of the fundamental concepts of this magneton theory from the chemical point of view from which Parson originally deduced them, but which has not yet been published in full.

According to Parson, the electron, or magneton as he calls it, is not a sphere, but a very thin ring, about 10^{-9} cm. in radius, around which the negative charge circulates at a very high speed, thus combining with its electrostatic properties the magnetic ones of a ring of wire carrying a current.

As Parson has shown, the magnetons in an atom will arrange themselves as far as possible in compact groups of eight. This grouping will explain the periodic table of the elements and the formation of all salts and other compounds whose bonds are electrostatic. The non-electrostatic bonds of organic compounds are explained as a result of magnetic attractions not strong enough to draw a magneton over from one atom into the other. Thus the theory covers a much wider range of chemical phenomena than previous ones, and even includes stability relations and the properties of the elements of the long periods. An added interest is given by the ability of this model to treat also such a widely different class of phenomena as those of radiation, referred to above, and those of optical rotation, for which the author has more recently found it an improvement over previous theories.

JEFFERSON LABORATORY,
HARVARD UNIVERSITY.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] Proc. Amer. Acad., Jan., 1915.

Ionization Potential of an X-Ray Tube.[1]

By E. C. Drew.

IN many recent publications the statement is made that the ionization potential of an X-ray tube is very much greater than the running potential, or in other words, it takes a much higher voltage to break down the resistance of the tube than it does to maintain the flow of current, once it is started.

An experimental invsetigation of the point has been made by the author with several standard type tubes. The current through the tube and the fall of potential across the tube are recorded by a loop oscillograph. The measurement of potential by an indirect method eliminates the objection to a direct one, viz: same current through the loop as through the tube. Each loop system is calibrated to read drop or current as required and the instantaneous values of the wave form are scaled off. From the values thus obtained, plots are made which indicate that the ionizing potential is not of the same order generally supposed. The law of current in the tube is not that of Ohm. The energy of ionization and the percentage that this bears to the total energy supplied is not the same in different types of tubes.

Randall-Morgan Laboratory of Physics,
University of Pennsylvania.

New Tests of Einstein's Photo-Electric Equation.[1]

By R. A. Millikan.

THIS paper contains the report of work on lithium of the same sort as that reported a year ago on sodium.[2] The apparatus is however new throughout. Planck's "h" appears as definitely in this work on lithium as it did in that on sodium. There is a very perfect linear relationship between PD and ν and the slope of the line gives

$$h = 6.585 \times 10^{-27},$$

which is within four tenths of one per cent. of the value found with sodium.

The long wave-length limit is found to agree accurately with the intercept on the ν axis of the $PD\nu$ curve.

The observed contact E.M.F. is not found to agree closely with the theoretical value $h(\nu_0 - \nu_0')$ but this may be accounted for by surface in homogeneities.

Einstein's equation is shown to lead to the conclusion that contact E.M.F. is independent of temperature, a result in agreement with recent experiments.

Ramsauer's conclusions are not wholly confirmed by these experiments. The causes for the discrepancies are pointed out.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] R. A. Millikan, Phys. Rev., Vol. IV., p. 74, 1914.

THE X-RAY SPECTRUM OF TUNGSTEN AT A CONSTANT POTENTIAL.[1]

BY DAVID L. WEBSTER.

IN the spectrum of a Coolidge tube at a constant potential, determined by Duane, Hunt and the author (see preceding paper) the distribution near λ_0 is especially significant. For if the rays were irregular disturbances, they would excite a reflection at any angle, the wave-length of the reflected rays being determined simply by the relative retardations of the waves from the different layers of atoms in the crystal, and the intensity by the extent of the fluctuations in the resulting disturbance; or, as in Schuster's analysis of white light, the intensity may be found from a Fourier series for the incident disturbance. Either way, there would be some intensity at any part of the spectrum.

The fact is, that the intensity is zero for all wave-lengths below the one whose quantum energy is the energy of the cathode particle, and that it suddenly begins to increase on passing that point. Therefore it seems that even in such a spectrum as this, where we are not concerned with any characteristic radiations, the X-ray vibrations are not irregular, but are sent out as trains of periodic waves of all frequencies below the critical one. This, like the evidence from absorption, shows the presence in the tungsten of oscillators of all frequencies. No oscillator can be started in vibration by a cathode electron that does not give it a whole quantum; nor can it take less than that from an electron and hold it until another electron arrives with more, although the production of secondary cathode rays by X-rays indicates that it can absorb continuously from them and store the energy until the quantum is acquired.

JEFFERSON LABORATORY,
HARVARD UNIVERSITY.

THE CORRECTION OF ECHOES IN THE AUDITORIUM AT THE UNIVERSITY OF ILLINOIS.[1]

BY F. R. WATSON.

AN investigation of the acoustical defects of the auditorium at the University of Illinois which has been in progress for a number of years was recently brought to a conclusion when materials were installed to correct the faults. A reverberation and echoes were found to exist. Experiments and calculations by Sabine's method gave means of determining the amount of sound-absorbing material necessary to correct the reverberation. Walls producing echoes were located by means of an arc-light backed by a parabolic reflector.[2] The arc gave forth a hissing sound that traveled with the light so that an observer could see where the sound struck. Small mirrors placed on the walls assisted in tracing the reflected sound.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] "Echoes in an Auditorium," PHYS. REV., Vol. 32, p. 231, 1911.

Experiments were then carried on in accordance with the analysis. Sounding boards of different sizes and shapes proved to be of small value.[1] Stretched wires[2] and ventilation currents[3] are apparently not effective as means of correcting acoustics. Canvases were hung in various positions in the auditorium to determine the effect of screening certain walls from the action of sound. Absorbing materials were also placed at critical places suggested by the analysis. The final provisional cure was brought about when four large canvases were hung in the dome.

From the acoustical standpoint the auditorium was then in fairly satisfactory shape. The canvas curtains, however, were unsightly and did not harmonize with the architectural features of the room. Steps were taken to find an arrangement that would satisfy both the acoustical and architectural requirements. Complications appeared from the fact that the amount of material necessary to cure the reverberation was insufficient to cover all the walls producing echoes; also, it was decided at this time to install a pipe organ, to change the lighting system and to redecorate the interior walls. Before deciding on the final cure, a preliminary experiment was tried whereby a large curved wall was covered with vertical strips of hairfelt 30 inches wide placed 30 inches apart with bare wall spaces between them. This arrangement had several advantages. It maintained the curvature of the wall and used only half the material necessary to cover the whole surface. Theoretically the incident sound would be broken up because the portions of the waves striking the felt strips would be strongly absorbed and changed in phase. The results obtained were encouraging so other walls were padded in a similar way except that the felt strips were installed one foot out from the wall.

The outcome has been generally satisfactory. The remodeled auditorium has been found to have acceptable acoustics for speaking, pipe organ music, orchestra and band concerts. Weak echoes due to unpadded walls have been reported in several instances but these do not appear to prevent the words of the speaker being understood. The author attributes the successful solution of the investigation in large part to the coöperation and suggestions of Professor James M. White, supervising architect of the university.

Detailed accounts of the investigation with numerous drawings and photographs may be obtained in Bulletin No. 73 on "Acoustics of Auditoriums," published by the Engineering Experiment Station of the University of Illinois, and in a later bulletin on "The Correction of Echoes" which will appear soon. These bulletins will be supplied on application to the author or to the director of the engineering experiment station, University of Illinois, Urbana, Illinois.

Laboratory of Physics,
University of Illinois.

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[1] "The Use of Sounding Boards in an Auditorium," Phys. Rev., Vol. 1 (2), p. 241, 1913. Also a more complete article in The Brickbuilder, June, 1913.

[2] "Inefficiency of Wires as a Means of Curing Defective Acoustics of Auditoriums," Science, Vol. 35, p. 833, 1912.

[3] "Air Currents and the Acoustics of Auditoriums," Eng. Record, Vol. 67, p. 265, 1913.

ON THE DISTRIBUTED CAPACITY OF SINGLE LAYER SOLENOIDS.[1]

BY J. C. HUBBARD.

THE periods of oscillation of circuits consisting of a single layer solenoid and an air condenser have been precisely measured by a method devised for the purpose by the author.[2] One of the objects of the measurements has been to determine the effective, or so-called distributed, capacity of solenoids, special attention being paid to the independent variation of all the factors upon which that quantity might depend. These are the diameter and axial length of the solenoid, the number of turns, the diameter of wire, and the dielectric effect of the insulation and of the core. The period of oscillation is given by

$$T = 2\pi\sqrt{L(K + K_0)},$$

where K is the capacity of the air condenser and K_0 is the remaining capacity of the system, *i. e.*, the capacity of leads and connections and the distributed capacity of the coil. Six values of K, ranging from 200 cm. to 1,500 cm. were used with each solenoid. The periods were measured to one part in two thousand and were of the order of 10^{-6} sec. With all the solenoids used the relation between T^2 and K is found to be linear within the errors of measurement, and accordingly the variation of L with the period is negligible. Hence, for a given solenoid, we may write

$$T^2 = Ka + b,$$

where $a = 4\pi^2L$, and $b = 4\pi^2LK_0$, from which, $K_0 = b/a$.

Since $K_0 = K_1 + K_2$, where K_1 is the capacity of the leads and K_2 is the distributed capacity of the coil, we have two independent means of finding K_2, once K_0 is determined for each solenoid. The first is by measuring the capacity of leads and connections, K_1, directly.[3] Whence $K_2 = K_0 - K_1$. The second is to make use of the fact that for geometrically similar electriacl system the electrical constants are in the ratio of the linear dimensions. Thus, if we take two coils, all the dimensions of one being n-fold greater than those of the other, we have, for one

$$K_0 = K_1 + K_2,$$

and for the other,

$$K_0' = K_1 + nK_2.$$

Whence,

$$K_0' - K_0 = (n - 1)K_2,$$

from which K_2 may be found. The results of the two methods are in close agreement. The values of K_2 for the coils used range from 5 to 30 cm. of capacity. The distributed capacity of a single layer solenoid measured in electrostatic units is found to be a number of the same order of magnitude as the radius of the coil, measured in cm., but shows relatively very slight variation with the axial length, number of turns, and diameter of wire. A detailed report of the investigation will shortly be published.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] PHYS. REV., N. S., I., p. 247, March, 1913.

[3] Loc. cit., p. 245.

Clark College,
Worcester, Mass.

An Equation of State for Normal Substances, Tested in the Vapor Dome.[1]

By Harvey N. Davis.

The equation discussed is

$$\left(p + \frac{a\phi(\theta)}{v^m}\right)(v - b) = RT,$$

the reduced form of which is

$$\left(\pi + \frac{\phi(\theta)}{\omega_0\omega^m}\right)(\omega - \omega_0) = \Delta_c\theta,$$

where

$$\omega_0 = \frac{m - 1}{m + 1}$$

and

$$\Delta_c = \frac{4m}{m^2 - 1}$$

are respectively the limiting reduced orthobaric volume and the ratio of the critical density to the density of a perfect gas, at the critical pressure and temperature. Van der Waals' equation, Dieterici's first equation of 1898, and Dalton's equation of 1914 are special cases of this type. The equation is tested for argon (Crommelin) and for eleven of Young's "thirty substances" selected to cover a wide range of behavior.

If any equation of this type is to be satisfactory, the observed ω_0's and Δ_c's must satisfy a certain relation obtained by eliminating m above. The twelve substances mentioned above, and some fifteen others are shown to satisfy this relation at least approximately, and probably within the limit of error of the observed ω_0's. It is therefore possible to select an m for each substance which will give substantially correct values for both ω_0 and Δ_c.

A partly new mathematical process is next discussed by which the reduced equation can be solved for saturation pressures, temperatures, and volumes, when the form of the function $\varphi(\theta)$ is preassigned. Conversely, one can determine from the experimental data a function $\varphi(\theta)$ that will give exact agreement for any one of the curves, π *vs.* θ, $\omega_{\text{vap.}}$ *vs.* θ (or preferably $\pi\omega_{\text{vap.}}/\Delta_c\theta$ *vs.* θ), and $\omega_{\text{liq.}}$ *vs.* θ (or preferably $\omega_{\text{liq.}}/\omega_{\text{vap.}}$ *vs.* θ, the latter forms being advantageous in that they do not depend on the observed critical volume). In what follows, the $\varphi(\theta)$ determined from vapor pressures will be used. It appears that it also gives excellent agreement on vapor volumes except in the neighborhood of the critical point. Even there the disagreement is small, and important only from the point of view of the kinetic theory. This $\varphi(\theta)$ will not, however, give as good predictions of *reduced* liquid volumes as will Dalton's equation (with $m = 2$ for all substances), even though Dalton's equation yields an ω_0 and a Δ_c which are greatly in error.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

The function $\varphi(\theta)$ is not the same for different substances, but can be put in the form

$$\phi(\theta) = 1 + k\,\Theta(\theta),$$

where the function $\Theta(\theta)$ is the same for all substances, and k is a constant appropriate to each substance. Furthermore, the k's of the twelve substances examined, when plotted against their m's, fall on a smooth curve within the probable limit of error of the critical volumes on which the m's depend. This smooth curve can also be made to pass through the point $k = 0$, $m = 2$, thus making van der Waals' theoretically derived equation one of the singly infinite family of equations that covers the range of real substances.

The fact that the k's form a single-valued function of the m's, means that one can predict with some accuracy the whole course of the reduced vapor pressure curve of a little investigated substance when only its critical virial coefficient is known. If one other point on the reduced vapor pressure curve, say the boiling point, had been available as a check on k, the accuracy of this prediction would have been of the order of a quarter of one per cent. in all but two of the twelve cases examined, and better than one per cent. in those two.

Conversely, it seems probable that the Δ_c of a substance can be predicted to better than one per cent. from its reduced vapor pressure curve. This possibility has not yet been carefully investigated, but it gives promise of developing into a method of determining critical volumes that will be somewhat more accurate and much more convenient than the law of the straight diameter.

A rather sensitive test of an equation of state is afforded by the accuracy with which it can predict latent heats. In this respect van der Waals' equation is very bad, Dieterici's somewhat better, and Dalton's better still. As regards numerical values, the new equation is even better than Dalton's over the observable range of the one substance examined by him, although the shape of the new latent heat *vs.* temperature curve is not quite as satisfactory as his.

Finally, it may be mentioned that this paper puts in an easily tested form an hypothesis already familiar to workers in this field, namely that the law of corresponding states, which is obviously untrue in its original form, is true if one gives it a single degree of freedom by introducing one disposable constant. In this paper the additional constant is the exponent m in the reduced equation of state, and it is found that, at least for ω_0's, Δ_c's, vapor pressures, and values of the ratio $\omega_{\text{liq.}}/\omega_{\text{vap.}}$, a one-dimensional law of corresponding states is in substantial agreement with the facts. Indeed the validity of such a law is, apparently, even greater than the validity of the particular form of equation of state that has been discussed.

The Jefferson Physical Laboratory,
Cambridge, Mass.

An Accurate Method for the Measurement of the Conductivity of Electrolytes.[1]

By W. A. Taylor and H. L. Curtis.

THE purpose of the work, which is now being carried on under a grant from the Carnegie Institution of Washington, to Dr. S. F. Acree, is to develop an accurate method for the measurement of the conductivity of electrolytes in both concentrated and dilute solutions. The work on the problem has been done at the National Bureau of Standards, of Washington, D. C., in order to have the benefit of their excellent apparatus in working out the details of the method. The investigation was begun by Dr. H. C. Robertson, working with Dr. S. F. Acree, at Johns Hopkins University, several years ago, but little definite data were obtained. At Dr. Acree's suggestion we took up three phases of the problem: first, the obtaining of a source of alternating current which is practically free from harmonics and whose frequency can be varied through wide limits; second, the construction of a suitable bridge; and third, the designing of satisfactory cells, and the study of the effect of changes in voltage and frequency on the resistance of electrolytes.

Several commercial generators giving frequencies of 500 cycles or above were tried, but in no case was the wave form sufficiently free from harmonics. A special high frequency generator made by the General Electric Company, giving frequencies from 600 to 3,000 cycles, was much better but did not entirely suit our needs. A Vreeland oscillator was finally adopted because it gives not only a pure sine wave but also an exceedingly steady frequency, which can be changed at will by means of suitable condensers. The oscillator now in use, for which we are indebted to the Leeds and Northrup Co., has a range of frequency of from 150 to 3,000 cycles. It gives a maximum voltage of 54 volts. This voltage is cut down by means of a transformer to voltages suitable for conductivity measurements.

An electrolytic cell behaves toward an alternating current as though it were made up of a capacity in series with a resistance. Hence when used in an alternating current bridge, it is necessary to compensate for this capacity either with inductance or capacity. The apparent capacity of an electrolytic cell is very large, being about 25 microfarads per square centimeter for bright platinum electrodes, and several times as large for platinized electrodes. Hence it is not feasible to compensate by adding capacity in series with an adjacent arm of the bridge. The compensation can be accomplished, however, by using a condenser in parallel with an adjacent arm, but for accurate work this condenser must have negligible losses. This is true only of air condensers and the range of capacity available is small. Hence the most satisfactory method is to use a variable inductance in series with the cell.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

To eliminate as many corrections as possible, a substitution method is employed as shown in Fig. 1. R_1 and R_2 are ratio coils of 100 ohms each, S is the resistance in the bridge, R a substitution resistance, C the cell, T the telephone and L a variable inductance. The resistance box R is set on zero, and with the cell in circuit, S and L are varied until there is no sound in the telephone. Then the cell is short circuited and the bridge again balanced by varying L and R. The reading of R is then the resistance of the cell. By working in this way we have found that, under favorable temperature conditions, measurements upon a cell will repeat to one or two parts in a hundred thousand.

The bath used to keep the cells at constant temperature is made of copper and filled with water and it was found that this caused a great source of error from capacity effects, as the value of the resistance in the bridge needed to balance the cell varied considerably, sometimes as much as 0.1 ohm, depending on whether the heating lamps of the bath were on or off. This source of error was eliminated by grounding the bath and also the bridge as in Fig. 1, when there was no difference in the two readings. It was found necessary to move the Vreeland and the transformer for cutting down the voltage to another room as their fields affected the bridge setting. Thus all high potentials should be kept as far as possible from the bridge.

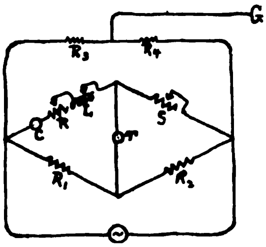

Fig. 1.

We first took up the problem of determining whether there is a change in resistance of a solution of an electrolyte with change in voltage. From the data obtained by the use of many different cells it was found that there is no measurable change in resistance with change in voltage, provided the cells, solutions, and the bottles used to hold the solutions are kept scrupulously clean. The slightest trace of grease or dirt, however, causes a change in resistance with change in voltage. This seems to be a good test for perfect conditions for measurements. The range of voltage was from 1/4 to 4 volts. Above this with the resistances used, the heating effect of the current prevented accurate measurements.

The next part of the work was to determine whether there is a change in apparent resistance with change in frequency. Cells with bright platinum electrodes, varying in size from one half to two inches in diameter were first studied. It was found, as is shown in the table below, that there is a change in resistance with change in frequency, and that this difference depends on the size of the electrodes, the largest electrodes giving the smallest change in resistance. Thus the two inch sand-blasted electrodes give a smaller change than any others.

The values for the inductance necessary to obtain a balance with the cell are also interesting. From an inspection of the following data it will be seen that as the difference in the resistance between 500 and 1,000 cycles increases the inductance also increases. The data shows one exception to this. It is also seen that the larger the electrode surface the smaller the inductance necessary for a balance.

Size of Electrodes.

	R 1,000 ~.	Ind. 1,000 ~.	Diff. in R at 500 and 1,000 Cycles in Per Cent.
½ inch bright	277.703	2,229	0.744
1 inch bright	310.202	425	0.110
2 inch bright	421.200	134	0.068
2 inch sand blasted	282.092	115	0.025
½ inch platinized	329.769	25	0.000
1 inch platinized	290.269	0	0.000
Decrease in Resistance of Solution.			
1 inch bright	310.202	425	0.110
1 inch bright	195.302	350	0.140
1 inch bright	82.834	445	0.477
1 inch bright	55.555	465	0.635
1 inch bright	41.042	550	1.024

These data also show that this change in resistance with change in frequency becomes smaller as the resistance of the solution is increased. This is no doubt due to the fact that we have an electrode effect which becomes a smaller factor as the resistance is increased.

We then took up the study of platinized electrodes. With a cell with one inch platinized electrodes no difference could be detected in the resistance measurements at 500 and 1,000 cycles. With one half inch platinized electrodes, however, we found in concentrated solutions, a small change in resistance with change in frequency, from 500 to 1,000 cycles, although this change was smaller than that for any of the cells with bright electrodes. It amounted to 14 parts in 100,000 for $N/5$ NaCl, but disappeared entirely with $N/20$ NaCl. In the platinized electrodes the surface is very much increased so that the change in resistance with change in frequency seems to depend directly on the size of the electrodes.

In order to try to eliminate this effect of change in resistance with change in frequency with bright electrodes, and thus get the true resistance of the solution in the cell, the following scheme was tried. Measurements were made at three different frequencies, 600, 1,000 and 2,000 cycles, with two cells, both of which had electrodes one inch in diameter, one set of which were bright and the other set platinized. Approximately $N/10$ and $N/20$ NaCl were used in each cell. We then plotted the results as a curve, using the resistance as ordinate and the reciprocal of the frequency as abscissa. By extending the curves to cut the *X* axis, we should get the resistances of the solutions at infinite frequency. Using the values of the resistances at infinite frequency we

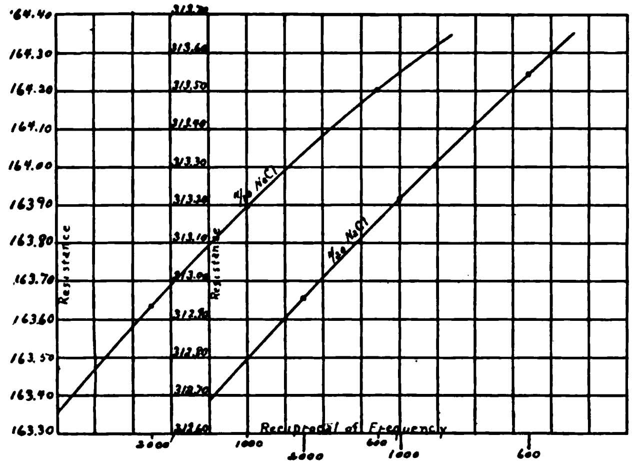

Fig. 2.

found the ratios of the resistances of $N/10$ and $N/20$ NaCl for each cell. For the cell with bright electrodes the ratio was 1.91417. For the one with platinized electrodes it was 1.91380. This shows a difference of about 0.02 per cent. or two parts in ten thousand in the two cells and a great part of this may well be due to experimental error, on account of poor temperature regulation, the poor sensitivity of the telephone at 2,000 cycles, error in plotting the curves, etc. From these and other similar measurements it would seem probable that the one inch platinized electrodes give the true resistance of the solution, and that we may be able to correct for the change in resistance with change in frequency with bright platinum electrodes, so that they can be used as well as platinized electrodes for making measurements of the conductivity of electrolytes, although perhaps with not so great an accuracy.

The work will now be continued under the direction of Dr. S. F. Acree at the University of Wisconsin.

NATIONAL BUREAU OF STANDARDS,
WASHINGTON, D. C.

A PROPOSED METHOD FOR THE PHOTOMETRY OF LIGHTS OF DIFFERENT COLORS.[1]

BY IRWIN G. PRIEST.

THE accompanying figure shows a horizontal plan of the proposed heterochromatic photometer. L_s and L_x are respectively the standard and the unknown lamp. L_c is the comparison lamp. L_c and L_s should be of the same color. S_1 and S_2 are opal glass screens. *L–B* is a Lummer-Brodhun cube. *O* is the ocular focused on *L–B*. *N* is a fixed nicol prism. *Q* is a right-handed quartz plate cut perpendicular to the optic axis and placed with its optic axis coincident with the line of sight, ZZ. It is mounted so as to be readily removable from and replacable in the path of the light. The best thickness of Q is to be determined by trial. N' is a nicol prism which can be rotated about the axis ZZ. C is a divided circle by means of which the rotation of N' can be measured. (It may also be desirable to use a collimating lens between S_1 and N and a lens between N' and $L-B$ to image S_1 on the side of $L-B$ remote from O.)

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

The procedure of making a measurement is as follows:

Q is replaced by a colorless homogeneous and isotropic glass plate of about the same refractive index. N' is set at 90° from its previously determined position for total extinction. L_s and L_c are balanced by sliding L_s along XX, L_c having been set at a convenient standard position. L_s is replaced by L_x and Q is replaced in the path ZZ. By sliding L_c and at the same time turning N', a ***complete match of both color and brightness*** is obtained.

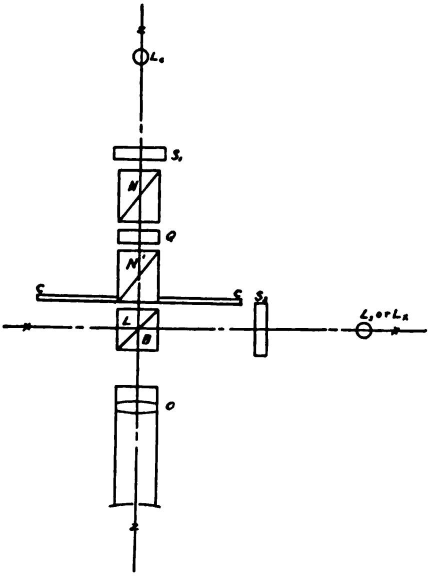

Fig. 1.

The candle power of L_x is computed as follows:

ϕ = angle through which N' was turned clockwise.

t = thickness of Q in millimeters.

T = transmission (ratio of emergent to incident light) of Q relative to the glass plate with which it is interchanged. (See above.)

R = ratio of brightness of S_1 when L_x is matched to its brightness when L_s is matched. (Determined by ordinary inverse square law.)

α_λ = specific rotation of quartz for light of wave-length λ.

V_λ = relative "visibility" of light of wave-length λ.

I_x = candle power of L_x.

I_s = candle power of L_s.

From ϕ, t, and the known rotatory dispersion of quartz compute the value of $V_\lambda \cos^2 (\phi - \alpha_\lambda t)$ for values of λ distributed through the visible spectrum. Plot $V_\lambda \cos^2 (\phi - \alpha_\lambda t)$ as a function of λ. Let S represent the ratio of the area of this curve to the area of the "visibility" curve.

I_x is given by

$$I_x = I_s \cdot R \cdot T \cdot S.$$

The computation can be very much simplified by the preparation of permanent tables showing $T \cdot S$ as a function of ϕ. Such tables should of course be based on the average of a large number of determinations of visibility, officially adopted as standard by consent of those interested.

This method has not been put into actual practice, but experiment[1] has demonstrated that, with such apparatus, using a quartz plate one millimeter thick, a perfect color match can be obtained between carbon and tungsten lamps, and that ϕ varies with the voltage on either lamp.

This idea is a "by-product" of other work the author is doing. Inasmuch as he is not in a position to have opportunity to put it into actual practice himself, he ventures to submit it to the consideration of others, without such detailed experimental work as would otherwise be considered necessary to precede its publication.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

A NULL METHOD WITH PHOTO-ELECTRIC CELLS.[2]

BY F. K. RICHTMYER.

FOR certain laboratory purposes where light sensitive devices of extreme sensitivity are desirable, photo-electric cells of sodium or potassium offer exceptional possibilities. At present the use of such cells as are ordinarily obtainable on the market is somewhat limited by the so-called "dark current." Improvements in construction, by Ives and others, have largely eliminated this source of error. But even in such cells where the so-called dark current is large the following arrangement completely eliminates it while not in the least reducing the sensitivity. Further, this arrangement makes possible for certain kinds of work a precision of measurement not available in any other way.

e_1 and e_2 are sources of potential difference, which can be varied independently at will from 0 to 120 volts. The $-$ terminal of e_1 and the $+$ terminal of e_2 are connected, in a sort of Wheatstone's bridge arrangement, to the photo-electric cells c_1 and c_2 respectively. Points b and b' are connected by a sensitive Dolazelac electrometer, and are also grounded, b' through a suitable make and break key k.

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[1] By use of the Arons Chromoscope. For description of this instrument see Ann. der Phy., 39, 545 (1912).

[2] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

Relative values of e_1 and e_2 may by trial be so chosen that the dark current through c_1 shall be equal to that through c_2 as shown by the null reading of the electrometer when k is open. (This critical ratio e_1/e_2 seems to be somewhat variable for any pair of cells. It depends on conditions not yet fully studied.)

If now c_1 and c_2 be illuminated by sources L_1 and L_2 at distances d_1 and d_2, respectively, either d_1 or d_2 may be so adjusted *that the resultant photo-electric currents are equal*, as is again shown by the null reading of the electrometer. This adjustment may be made with a very high degree of precision, even with the simple cells obtainable on the market. One might call such an arrangement a "differential photo-electric photometer," since the sensitivity is limited only by the *absolute* difference (photo-electrically measured) in the two illuminations, and not by their relative difference, as is the case with visual photometers. In fact such an arrangement is to light measurements what the Wheatstone's bridge is to resistance measurements.

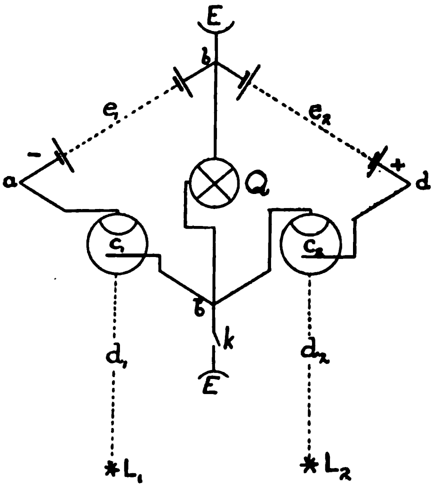

Fig. 1.

For various positions of L_1 there are corresponding positions of L_2 for a "balance." The following two sets of data give some idea as to the precision available.

If d_1 be plotted against d_2 a rigorously straight line results (not passing through the origin because in the particular apparatus used the positions of L_1 and L_2 were read on scales whose zero did not quite coincide with the sensitive surface).

These straight lines show that the two cells in question obey *exactly* the same current-illumination law, and further that this law must be a simple exponential one of the form

$$C = k \cdot I^x,$$

where C is the photo-electric current, I is the intensity of illumination, and x

L_1 and L_2 were 8 c.p. tungsten lamps.

Set 1. $e_1 = 28$ Volts, $e_2 = 36$ Volts.		Set 2. $e_1 = 47.2$ Volts, $e_2 = 52.8$ Volts.	
d_1	d_2	d_1	d_2
438.2 cm.	235.4	404.6	228.4
369.8	199.0	375.6	212.5
288.8	156.7	330.0	187.2
249.8	135.7	260.0	148.1
205.7	112.5	220.0	125.8
175.8	96.6	190.0	109.0
123.9	68.9	170.0	97.6
		155.0	89.3

is an exponent, which, according to previous observation is probably equal to unity. Indeed on the basis of the present experiment alone, it can hardly be anything else. Further work along this line is in progress.

There are many obvious applications of the above arrangement, particularly where small differences in illumination are to be measured or detected. The preliminary observations thus far made indicate that, so far as the photoelectric cells are concerned, differences in illumination of .01 per cent. are measurable. The sensitivity can be further increased many times by using more sensitive cells, better insulation, etc.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY.

THE VISIBILITY OF RADIATION IN THE RED END OF THE VISIBLE SPECTRUM.[1]

BY EDWARD P. HYDE AND W. E. FORSYTHE.

THE visibility of radiation has been determined in a number of investigations among which may be mentioned particularly those of König,[2] Ives[3] and Nutting.[4] The two principal methods that have been employed are those of "equality of brightness," and "flicker," and the measurements have extended from 0.4 μ to 0.7 μ, though the data near these limits, as determined by Nutting, who has carried his measurements further than any other observer, are given only to one significant figure.

In connection with a problem in optical pyrometry recently investigated in this laboratory it was important to know the sensibility curve of the eye somewhat beyond 0.7 μ and to be certain of the values to a reasonable degree of accuracy. To this end the present investigation was undertaken, making use of an adaptation of the arrangement employed in the Holborn-Kurlbaum optical pyrometer. The advantage of the method of optical pyrometry lies in the availability of greater brightness, which permits the extension of measurements further toward the ends of the spectrum. Although, in accordance with our present needs measurements were confined to the red end of the spectrum, the method might be employed also in extending the sensibility curve in the short wave-lengths.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] König, Gesammelte Abhandlungen.

[3] Ives, Phil. Mag., Dec., 1912, p. 853.

[4] Nutting, Phil. Mag., Feb., 1915, p. 301. See also Bender, Ann. d. Phys., *45*, p. 115, 1914.

In Fig. 1 is shown the apparatus used. The spectrum of a broad vertical carbon filament (*A*) is formed by means of a Hilger constant deviation spectrometer in the focal plane of the telescope object-glass, in which plane is placed the horizontal filament of a second lamp (*F*). A lens (*H*) projects an image of this filament and of the background spectrum on a narrow vertical slit (*I*) in the focus of the eye-piece (*J*). By rotating the drum-head of the spectrometer any spectral region may thus be brought into the field of view and compared in intensity with the pyrometer filament operated at a constant current. Rotating sectored disks placed between the carbon filament (*A*) and the colimator slit (*C*) of the spectrometer and quite close to the latter served to reduce the apparent brightness in the more luminous regions of the spectrum, the final settings being made by turning the drum-head of the spectrometer.

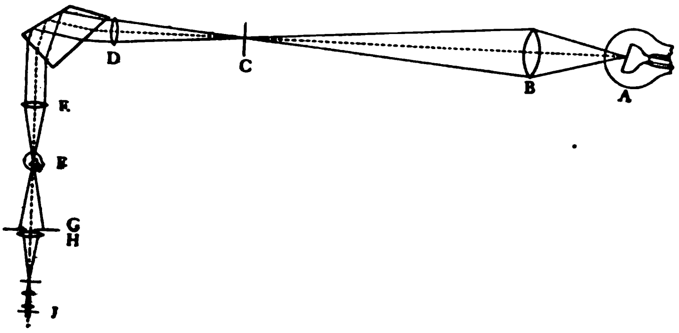

Fig. 1.

The energy curve of the broad-filament carbon lamp (*A*) was determined by comparison with a black body. In reducing the observed luminosities, corrections were made for dispersion, slit-widths, selective absorption of the lenses and prism, and scattered light. The illumination of the retina was well beyond the region of the Purkinje phenomenon, and the size of the field was extremely small, corresponding to a 2 mil filament magnified 6 times by the eye-piece.

Measurements made by 9 observers gave the average results shown in the accompanying table. In the second column are given the relative ordinates of the mean visibility curve of the 9 observers, taking the ordinate at $\lambda = 0.650\mu$ equal to unity. In the third, fourth and fifth columns are given the corresponding data of Nutting, Ives and König, as far as they overlap. The "equality of brightness" method was used in the determinations by

König and the "flicker" method by the other investigators. Our own data are given between the limits $\lambda = 0.630\,\mu$ and $\lambda = 0.770\,\mu$. It is quite practicable to extend the limit somewhat further into the red if there is any reason for it, and measurements might be made through the more luminous region of the spectrum and further into the blue than any previous measurements. It was, however, apart from our immediate purpose and hence was not undertaken.

The agreement between our values and those of the other investigators within the common region is as good as could be expected. The agreement among the different observers in our measurements in the red is probably better than that attainable in the more luminous region of the spectrum where the color differences are much more pronounced. It should be remembered that the agreement referred to pertains to the relative visibility in different wave-lengths of the red region rather than to the visibility in the red region compared with the visibility of white light, which was found to be markedly different for different observers.

Visibility Data on 9 Subjects in the Red End of the Spectrum.

Wave-lengths.	Mean Visibility of 9 Subjects.	Mean Values Given by Nutting.	Mean Values Given by Ives.	König's Values.
0.630	280	265	262	234
.640	170	160	168	164
.650	100	100	100	100
.660	53	54	65[1]	55
.670	27	30	42[1]	25
.680	13	13	25[1]	
.690	6.3	7.5		
.700	3.2	2.0		
.710	1.6			
.720	.79			
.730	.39			
.740	.19			
.750	$.09_5$			
.760	$.04_5$			
.770	$.02_0$			

[1] Extrapolated values.

THE EFFECTIVE WAVE-LENGTH OF TRANSMISSION OF RED PYROMETER GLASSES AND OTHER NOTES ON OPTICAL PYROMETRY.[1]

BY EDWARD P. HYDE, F. E. CADY AND W. E. FORSYTHE.

A. THE EFFECTIVE WAVE-LENGTH OF TRANSMISSION OF RED PYROMETER GLASSES.

IT is common practice to employ so-called monochromatic glasses in the eye-piece of an optical pyrometer. Among the glasses commonly used are Jena "Kupferrubin" glass No. F-2745 and Jena "Rotfilter" No. F-4512.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24, 1915.

The transmission of a specimen 2.9 mm. thick of what is supposed to be the "Rotfilter" glass is shown in curves (*a*) and (*a′*) in Fig. 1. The transmission of two thicknesses of the glass (5.8 mm.) in the visible spectrum is given by the curve (*b*). It is seen that the transmission band is rather broad, though the apparent breadth, as observed with a spectroscope, is much less owing to the limit of vision. It has been recognized by Waidner and Burgess,[1] Pirani[2] and others that, owing to the breadth of the transmission band, the effective wave-length of monochromatic light is subject to change with change in spectral distribution of the incident radiation, as occasioned by changes in temperature of the radiating source under investigation.

Attempts have been made to determine the effective wave-length of monochromatic light for various specimens of pyrometer glass by estimation of the wave-length of maximum luminosity in the prismatic spectrum of a source observed through the glass screen, and Waidner and Burgess[3] have attempted to show how this wave-length changes with a change in the temperature of the source used. This method of determining the effective wave-length is subject to criticism on two grounds. First, the wave-length of maximum luminosity determined in this way is not, in general, the center of gravity of the luminosity curve of transmission; and, secondly, the wave-length corresponding to the center of gravity in any region of temperature is not of particular significance, but rather that wave-length, such that for any definite temperature interval the ratio of the radiation intensities in that wave-length shall equal the ratio of the integral luminosities through the glass screen.

Various values of effective wave-length of monochromatic light for the red glass screens used with the Holborn-Kurlbaum pyrometer have been used, the determination of this wave-length having been made in the ways indicated above. A value as low as 0.658 μ has frequently been used. Moreover, Waidner and Burgess by their method outlined above, found that the effective wave-length seemed to become longer at higher temperatures,—a result quite contrary to expectation. Owing to the importance of knowing the effective wave-length in accurate measurements in pyrometry the present investigation was undertaken, using a double thickness (5.8 mm.) of the best, or most nearly monochromatic glass in our possession, viz., that for which the transmission curve is given in Fig. 1, and probably of the kind known as Jena "Rotfilter" No. F–4512.

It was desired to determine the effective wave-length between two definite temperatures of a black body, and to determine how this effective wave-length changes as the temperature interval is changed. Two methods were employed: (1) that of direct measurement; and (2) that of computation, assuming a knowledge of the visibility curve of the eye. An electric incandescent lamp at two arbitrary currents, corresponding in energy distribution to a black body at 1600° K. and at 2000° K. respectively, was selected as the source, and the measurements were made using a double thickness of glass (5.8 mm.), as this thickness of glass is usually used.

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[1] Bull. Bur. of Stnd., *3*, p. 163, 1907.

[2] Verh. d. Deut. Phys. Ges., *15*, p. 826, 1913. See also ibid. *17*, p. 47, 1915.

[3] Loc. cit.

By the first method, the ratios of emission intensities of the source for a number of wave-lengths at the two temperatures were measured, and these ratios compared with the ratio of integral luminosities of the radiation from the source observed through the double thickness of glass. These measurements were carried out with two distinct sets of apparatus. In one set of measurements the ratios of the radiation intensities were measured with a spectro-photometer, and the integral luminosities were determined with a Lummer-Brodhun photometer having the double thickness of red glass in the eye-piece. In the other set of measurements the ratios of the radiation intensities were determined with a spectral pyrometer, and the ratios of the integral luminosities were measured by the use of a laboratory form of the ordinary Holborn-Kurlbaum pyrometer having two thicknesses of the red glass in the eye-piece.

By the second method the integral luminosities through the red glass at the two chosen temperatures were computed from a knowledge of the spectral energy curves (computed from Wien's equation), the transmission curve for the glass (Fig. 1, curve (*b*)), and the sensibility curve of the eye. Inasmuch as the best published visibility data extend only to 0.7 μ and are only given to one significant figure in this region, which is most important in the present investigation, a preliminary investigation of the sensibility of the eye in this region was undertaken.[1] The data obtained in this preliminary investigation were used in the present computations.

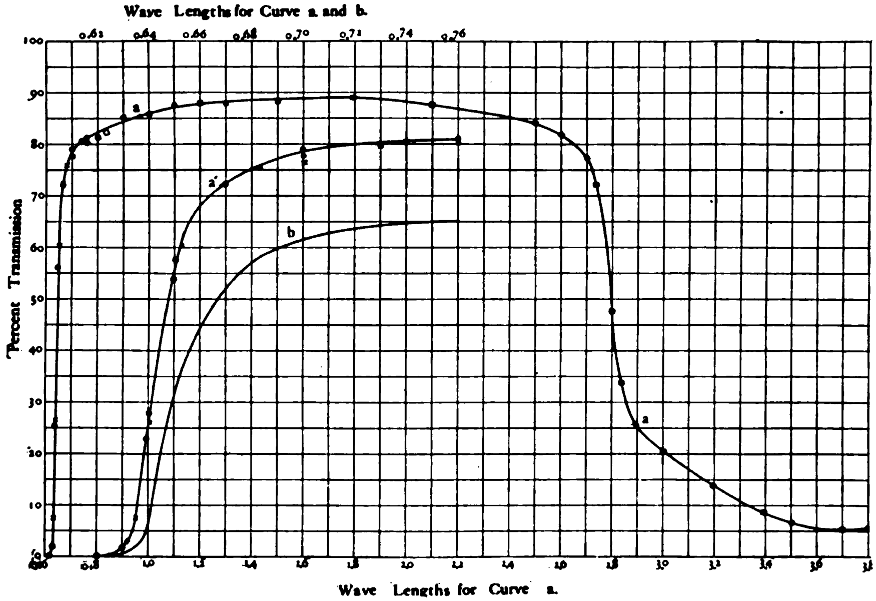

Fig. 1.

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[1] See previous abstract.

The results obtained by the two methods of direct experiment and by the method of computation are given in Table I.

Table I.

Effective Wave-Length of Monochromatic Transmission for Two Pieces of Red Pyrometer Glass, 5.8 mm. Total Thickness, Between the Temperatures 1600° K. and 2000° K.

Direct experiment, using spectrophotometer	$0.664\ \mu$	$\pm\ 0.001\ \mu$
Direct experiment, using pyrometer	0.663_6	$\pm\ 0.001$
Computed value	0.663_8	
Mean	$0.664\ \mu$	$\pm\ 0.001\ \mu$

The next point of interest lies in the variation of this effective wave-length with change in temperature in the source studied. These variations can be determined most accurately by the method of computation, and as the changes in effective wave-length are small it is unnecessary to give the value for more than a few temperature intervals. In Table II. are given the results of these computations, assuming the effective wave-length between 1600° K. and 2000° K. to be the mean value given in Table I.

Table II.

Computed Changes in the Effective Wave-Length of Transmission of Two Thicknesses (5.8 mm.) of Red Pyrometer Glass for Various Temperature Intervals.

Temperature Interval.		Effective Wave-length.
1336° K.–1600° K.		$0.664_9\ \mu$
1600° - 1822°		0.664_1
1822° - 2400°		0.662_9
2400° - 3100°		0.661_7
1336° - 1822°	(Gold to palladium)	0.664_6
1336° - 3100°		0.663_4

Observations made on other pieces of glass used with the Holborn-Kurlbaum and other pyrometers indicate quite appreciable deviations from the particular specimen studied in the present investigation. As obviously it would be inconvenient to subject every sample of glass to such an investigation as recorded here, it appears desirable to find a simple way of calibrating glasses in terms of the specimen here investigated. This can be done readily, by determining the ratio of the apparent candle-power of a standard lamp at two definite currents, using the glass under investigation in the eye-piece of a Lummer-Brodhun or other suitable photometer, and comparing this observed ratio with the known ratio as determined with the known sample of glass in the eye-piece of the photometer. If the ratio with the test glass is found to be, say 1 per cent. greater than the given ratio for the standard glass, then the effective wave-length for the temperature interval corresponding to the two currents through the lamps must be shorter than the accepted wave-length of the standard glass by an amount readily computed from Wien's equation of spectral energy distribution, and from the known black body "color match" temperatures of the lamp at the two currents. Until the standardization of glasses may be undertaken by the Bureau of Standards, Nela Research Laboratory will be glad for the convenience of other investigators to calibrate red glasses in terms of our standard, or else will, if desired, furnish at cost lamps calibrated between two definite currents, giving the black body "color match" temperatures and the ratio of apparent candle-powers as determined with the standard red glass in the eye-piece.

B. THE TEMPERATURE COEFFICIENT OF TRANSMISSION OF RED PYROMETER GLASS.

In connection with the investigation described above it was observed that the transmission of the red pyrometer glass, presumably made with copper oxide, and dependent for its color on a colloidal solution, is subject to a large change with temperature. This has not been investigated thoroughly, but observations were made at two temperatures 20° C. and 81° C. by immersing the glass in water heated to these two temperatures. The results are given in Fig. 2. Curve (*a*) is the transmission of the glass at the lower temperature 20° C., and curve (*b*) the corresponding curve at the higher temperature 81° C. The transmission is shown to decrease with increase in temperature, the coefficient of temperature change being greatest in the shorter wave-lengths. The change is such as to make the transmission band appear to shift to longer wave-lengths as the temperature is increased. A further investigation of this should give data with which to test the theoretical formula of Mie[1] for colloidal solutions.

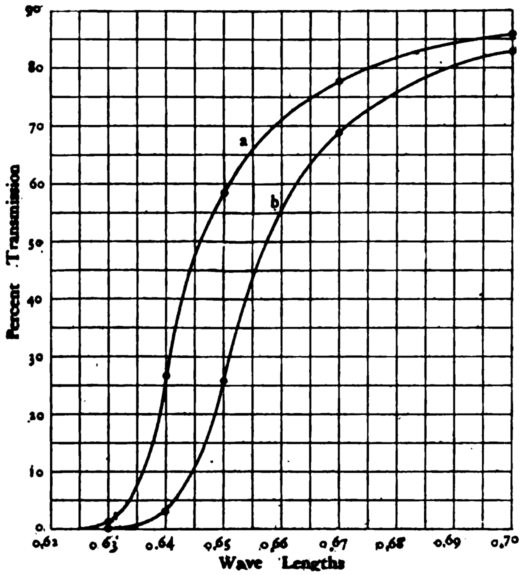

Fig. 2.

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[1] Ann. d. Phys., *25*, p. 377; 1908.

C. INFLUENCE OF POSITION OF ROTATING SECTORED DISK IN USE WITH THE HOLBORN-KURLBAUM TYPE OF PYROMETER.

If a rotating sector is used with an optical pyrometer to reduce the intensity of the source, care must be taken as to the location of the sector. There is a very marked difference in the results of temperature measurements depending upon whether the sector is located near the projection lens or as near as possible to the pyrometer lamp. There is also a difference depending upon the relative position of the openings in the sector and the source providing the source consists of a lamp filament. If a sector of small transmission is mounted near the lens and so placed that the openings of the sector are parallel to the axis of the filament when passing across the center of the lens, the definition is very bad while if the openings of the sector are turned through 90° so that they are perpendicular to the axis of the filament, the definition is quite good. When the rotating sector is located near the pyrometer lamp the definition is good and independent of the position of the openings of the sector. If a very large source, as for example a black body, is used no such effect is to be noted.

If a lamp filament used as a background be set so that it has the same brightness as a black body at 1822° K. (the temperature of melting palladium) as determined by the optical pyrometer using red glass before the eye-piece and this background again set at the brightness corresponding to the melting point of gold as indicated by the black body, the relation between these two lamp brightnesses as determined by the rotating sector if placed near the projection lens is not the same as that for a black body over the same range. The differences are relatively small when the sectored disk is mounted near the pyrometer lamp.

Nela Research Laboratory,
National Lamp Works of General Electric Co.,
Nela Park, Cleveland, O.,
April, 1915.

ANEROID BAROMETERS.[1]

By M. D. Hersey.

A PRIMITIVE type of aneroid barometer was invented in 1798 to meet the needs of aeronautics at the time. The present activity in aviation has again directed attention to the difficulties involved in the accurate use of this instrument. The first aneroid was found to be worthless on account of temperature effects. It was forgotten, and in 1847 a successful aneroid was independently invented. This later aneroid did not have its vacuum box so completely exhausted; consequently, the expansion of the confined air with rising temperature just compensated for the diminishing stiffness of the metal.

The aneroids at present in use differ only in details from that of 1847. During the ten years following this date a number of new types of mechanism appeared, including the Bourdon aneroid (apparently the precursor of the Bourdon pressure gage), and the Goldschmid aneroid (which dispenses with the fragile lever system, readings being taken with a micrometer screw). Then, as contributions to the mechanical development of the aneroid fell off, the frequency of published articles on the accuracy of aneroids rapidly increased. A great many such articles appeared about 1880. These investigations would usually end by announcing that, under good conditions, the "probable error" of an aneroid is a certain number of hundredths of a millimeter.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

About 1890 an important investigation by the late explorer, Edward Whymper, showed that errors of a thousand feet (some 20 millimeters on the pressure scale) might occur in the practical use of aneroids at high altitudes, owing to their inherent tendency to "creep" or drift in their indications when held at a constant low pressure. Chree, in 1898, published a statistical study of aneroid tests and experiments at Kew Observatory; expressing the numerical magnitude of this drifting effect, in its several manifestations, by empirical equations. But these interesting figures were not accompanied by a sufficient description of the mechanical details of the aneroids to enable us to trace the errors to their sources; in a word, he investigated the dependent, but not the independent variables of the problem. Immediately after this, Prof. C. F. Marvin, on the basis of certain experiments, urged the need of a physical study of the aneroid, and, in particular, of the vacuum box. Important additions to the available data are also to be found in the publications of the Physikalisch-Technische Reichsanstalt.

However, all this material is fragmentary, and, in itself, inadequate to answer the two questions confronting the Bureau of Standards, viz.: What specifications will insure the selection of a good aneroid for a particular purpose? and, How shall aneroids be tested in order to get corrections that are applicable in practical use? Consequently, four years ago, the Bureau undertook a general experimental study of the accuracy of aneroid barometers. Certificate blanks have recently been issued[1] containing a provisional set of specifications and method of testing. From time to time these will be revised.

In the course of the investigation the following points have been considered:

1. The coördination of existing data.
2. Recognition of the physically distinct uses to which aneroids are put.
3. Defects frequently met although readily avoidable.
4. The classification of errors and determination of characteristic curves showing their variation with conditions, viz.:
    I. Transient errors: including effects of temperature lag, etc.
    II. Inherent errors: including those due to looseness, friction, lack of balance, elastic after effect and hysteresis, thermal expansion, temperature change in elastic modulus and hysteresis, etc.

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[1] The Bureau has also published a Circular (No. 46) on The Testing of Barometers. This circular, which is equally concerned with mercurial and aneroid barometers, is written for the guidance of persons who are already familiar with the use of such instruments and wish them standardized at the Bureau. A brief enumeration of the defects and errors to be guarded against is followed by a schedule of fees for the various tests.

III. Secular errors: including effects of pressure oscillations, of shocks received in transportation, and of age alone.

5. The localization of sources of error:
    (*a*) Statistically, correlating errors with constructive details;
    (*b*) Physically, isolating the parts and observing their separate action.

6. A comparative test of a number of representative aneroids to determine the degree of accuracy reasonably attainable.

7. Comparison of relative merits of diverse types of construction.

8. Comparison of results of different methods of testing; including a study of the seemingly contradictory reports furnished by the government laboratories of England, France, and Germany on two aneroids taken abroad in 1913.

9. Mathematics of the action of an ideal aneroid, *i. e.*, one conceived to be free from sources of error; a necessary preliminary to any discussion of improvements in design.

10. Possible errors of barometric altitude estimation due to wind, moisture, and temperature irregularities in the air column.

In conclusion, it appears that errors which might otherwise mount up to 5 or 10 per cent. can usually be kept down to 1 or 2 per cent. by the intelligent selection and use of an aneroid for a given purpose.

A METHOD OF MEASURING HEAT CONDUCTIVITIES.[1]

By R. W. King.

UNDER the *boundary conditions*

$$\theta(o, t) = \theta_1 + \theta_2 \cos \omega t,$$
$$\theta(\infty, t) = o,$$

the solution of the differential equation expressing the linear flow of heat is

$$\theta = \theta_1 e^{-p_1 x} + \theta_2 e^{-p_2 x} \cos (\omega t - qx)$$

where

$$q = \sqrt{\frac{k}{2}}\sqrt{-\mu + \sqrt{\mu^2 + u^2}},$$

μ being the radiation constant per unit of length and k the thermal conductivity divided by the product of density and specific heat. Thus it is seen that the velocity of propagation of the impressed heat wave depends, among other things, upon ω and μ; and it is possible, by determining experimentally the velocities corresponding to ω_1, ω_2 in a rod for which μ remains constant, to eliminate μ and express k in terms of ω_1, ω_2, v_1, v_2, the density and specific heat.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

The experiment here indicated has been performed upon metal wires about 2.5 mm. in diameter and from 25 to 40 cm. in length, the first boundary condition being maintained by inserting one end of the wire in a small heating coil through which was caused to flow a current whose value is given by the expression

$$I = I_0 \left| \sin \frac{\omega}{2} t \right| ,$$

and the second boundary condition being maintained through radiation. The velocities of propagation were determined by noting the time lag between the motions of two short-period galvanometers connected with thermocouples, these couples being attached a few centimeters apart to the end of the wire at which heat is applied.

The materials thus far worked with have been copper and tin, and sample results are shown in the following table.

Copper.			Tin.		
Period in Seconds.	Time Lag in Seconds.	Conductivity in Absolute Units.	Period in Seconds.	Time Lag in Seconds.	Conductivity in Absolute Units.
130.7 293.0	11.77 15.52	.910	129.7 290.0	11.30 14.36	.1551
129.3 291.3	12.12 16.60	.907	130.1 294.5	11.41 14.66	.1543
129.8 293.0	12.26 16.97	.906	128.3 287.7	11.22 14.31	.1553

By enclosing the test piece and heating coil in an electric furnace, the conductivity of copper at 360° C. was found to be 0.858.

The method would thus seem to permit of an extension to high and low temperature work, and measurements of this nature are soon to be attempted. Whether or not it can also be utilized in measurements upon poor conductors has not yet been determined.

DEPARTMENT OF PHYSICS,
CORNELL UNIVERSITY.

A Theory of Adsorption.[1]

By Irving Langmuir.

BRAGG has shown that the atoms of crystals are arranged according to a space lattice, the identity of the molecules being lost. The forces acting between the atoms are thus chemical forces. In the case of diamond, the tetravalent character of carbon is manifest from the structure, but in most cases the valency appears to be *divided* between several atoms. Thus in sodium chloride the single valency of the sodium atom is divided between six chlorine atoms. There is a close connection between this theory and Werner's theory of valence.

On the surface of a crystal there must be unbalanced forces, so that the atoms may be considered to be in an unsaturated state. This is thought to be the cause of adsorption. An adsorbed film thus consists of atoms (or molecules) of the adsorbed material chemically held by the atoms of the solid so as to form a continuation of the space lattice of the solid. The surface of a crystal is thus looked upon as a checkerboard containing a definite number of spaces, each space capable of holding one atom (or molecule) of the adsorbed substance.

The amount of material adsorbed depends upon a kinetic equilibrium between the rate of condensation and the rate of evaporation from the surface. Practically every molecule striking the surface condenses (independently of the temperature). The rate of evaporation depends on the temperature (Van't Hoff's equation) and is proportional to the *fraction* of the surface covered by the adsorbed material. Molecules striking a surface already covered also condense, but usually evaporate much more rapidly than from the first layer. Hence, except where the vapor is nearly saturated, the amount of material adsorbed on a *plane surface* rarely exceeds that contained in a layer one atom (or molecule) deep.

This theory is based on and seems to be in good accord (both qualitative and quantitative) with phenomena of:

1. Electron emission from heated metals.
2. Photoelectric effect.
3. Kinetics of heterogeneous chemical reaction (catalysis).
4. Electrochemical action, especially polarization and passivity.
5. Evaporation.
6. Heat conduction in gases at low pressures.
7. Adsorption.

Passivity.—According to this theory, a metal electrode in an aqueous solution is nearly completely covered with hydrogen and oxygen atoms (or OH radicals), chemically combined with the metal atoms, thus forming a layer one atom or molecule deep. In the case of metals such as platinum, the rate at which the oxygen atoms leave the surface (evaporate into the solution) is large, compared to the rate at which the hydrogen atoms evaporate, whereas with metals like iron and nickel the reverse is true. A layer of oxygen atoms renders the surface passive, while hydrogen renders it active. Hydrogen may destroy the oxygen layer and remove passivity.

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[1] Abstract of paper presented at the Washington meeting of the Physical Society, April 24, 1915.

This theory seems to combine the advantages of Faraday's oxide theory, Le Blanc's reaction velocity theory, Foerster and Schmidt's hydrogen activation theory, and Reichinstein's constant-sum theory (this latter because of the definite number of spaces available on the surface of the electrode).

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THE

PHYSICAL REVIEW.

THE INDEX OF REFRACTION OF GASES.

By Janet Tucker Howell.

A NUMBER of laws have been formulated to express the relation between the index of refraction of a substance and its density. Gladstone and Dale[1] first proposed the empirical relation

$$\frac{\mu - 1}{d} = \text{constant}.$$

This equation is the one most generally used as it holds within experimental error for the range of densities usually investigated. The most serious rival to the law of Gladstone and Dale is the relation proposed by H. A. Lorentz;[2] namely,

$$\frac{\mu^2 - 1}{(\mu^2 + 2)d} = \text{constant}.$$

For gases, at low pressures, this amounts to the same thing as the law of Gladstone and Dale, since μ is so nearly equal to 1.

$$\frac{\mu^2 - 1}{(\mu^2 + 2)d} = \frac{(\mu - 1)(\mu + 1)}{(\mu^2 + 2)d} = \frac{2}{3}\frac{\mu - 1}{d}.$$

But at sufficiently high pressures it should be possible to tell which law is better. This has been tried by several investigators, but with discordant results.

Mascart,[3] using an interference method, found that, for air, $\mu - 1$ increased more rapidly than the pressure.

Chappuis and Rivière[4] found that, for air and carbon dioxide, $\mu - 1$ is proportional to the density up to 20 atmospheres.

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[1] Phil. Trans., p. 887, 1858; p. 317, 1863.

[2] Lorentz, Theory of Electrons, p. 143.

[3] Comptes Rendues (78), p. 617, 1874.

[4] Ann. de Chim. et de Physique (14), p. 5, 1888.

Carnazzi,[1] working with a prism, found that $(\mu - 1)/d$ increased for air and decreased for carbon dioxide as the pressure was increased.

Gale,[2] with a modification of the Jamin refractometer, found that, for air, there is no more than .1 per cent. departure from $(\mu - 1)/d =$ constant, up to 20 atmospheres.

Magri[3] measured the refractive index of air by means of a Jamin refractometer, varying the pressure from 1 to 176 atmospheres. Comparing $(\mu - 1)/d$, $(\mu^2 - 1)/d$, and $(\mu - 1)/((\mu^2 + 1)d)$, he found that the last function is the only one that remains constant.

This work was originally undertaken with the intention of investigating the effect of density on the index of refraction of several gases, up to 200 or 300 atmospheres. Owing to the difficulty of constructing a bomb for holding the interference apparatus that was capable of standing such high pressures, these experiments were delayed and the work reported here was carried out as a preliminary investigation. It is an attempt to extend the dispersion curves of several gases as far as possible into the ultra-violet, as the method employed is admirably suited to this work. This method, involving the use of a Fabry and Perot interferometer in connection with a spectroscope, has several advantages over the usual method with the Jamin refractometer for certain fields of work. The temperature can be more easily controlled, and, since it is not necessary to count the number of interference bands going by for a change of pressure of an atmosphere, it is possible to work in the ultra-violet region. Miss Matthews[4] used this method in investigating the effect of change of temperature on the index of refraction at constant pressure and found it very satisfactory.

A great deal of work has been done on the indices of refraction of gases in the visible spectrum—the most recent being that of C. and M. Cuthbertson. Using a Jamin refractometer they determined the indices of refraction of air, oxygen, nitrogen, hydrogen,[5] neon,[6] krypton, xenon, helium, and argon,[7] between λ 6563 and λ 4861.

Rentschler,[8] using a Fabry and Perot interferometer and a concave grating, determined the indices of refraction of air, nitrogen, oxygen, carbon dioxide and carbon monoxide, from λ 5769 to λ 3341. His interferometer plates were silvered and, as the reflecting power of silver is low between λ 2280 and λ 3150, he was unable to extend his readings any further.

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[1] Il Nuovo Cimento (6), p. 385, 1897.

[2] PHYS. REV. (14), p. 1, 1902.

[3] Phys. Zeitschr. (6), p. 629, 1905.

[4] Journal of the Franklin Inst., p. 673, June, 1914.

[5] Proc. Roy. Soc. (83), p. 151, 1909.

[6] Proc. Roy. Soc. (83), p. 149, 1909.

[7] Proc. Roy. Soc. (81), p. 440, 1908.

[8] Astro. Jour. (28), p. 345, 1908.

With interferometer plates nickeled by cathode discharge, and by using a Fabry and Perot interferometer in connection with a quartz spectrograph, I have been able to extend the dispersion curve of air to λ 2652 and those of hydrogen, oxygen, and carbon dioxide to λ 2753. From the values found for the indices of refraction the dispersion formulae of these gases were calculated by the method of least squares.

Apparatus.

The apparatus is shown in Fig. 1. Light from the source *S* is focused on the quartz window *A* of the tube *H* containing the interferometer plates *C*, by means of the quartz lens *L*. The tube *H* is immersed in a constant temperature oil bath *B*. A lead pipe *M* leads to a manometer and pump so that the pressure can be changed and read. The temperature seldom varied more than .05° C. during an exposure and with air, the pressure was kept constant to within 2 mm. With the other gases it was found more difficult to regulate the pressure, but the change during an exposure was never greater than 1 cm. and usually much less. The interferometer *C* consists of two plane parallel quartz plates nickeled by cathode discharge. They are separated a constant distance *d* by an etalon so that $2d = .952$ cm. approximately. After passing through the interferometer plates, the light goes through the quartz window *A′*, is turned by the right-angled quartz prism *D* so that it falls on the concave speculum mirror *E* which brings the ring system to a focus at *F*. *F* is the slit of a Hilger quartz spectrograph, size *c*, giving a spectrum 200 mm. long from λ 2100 to λ 8000.

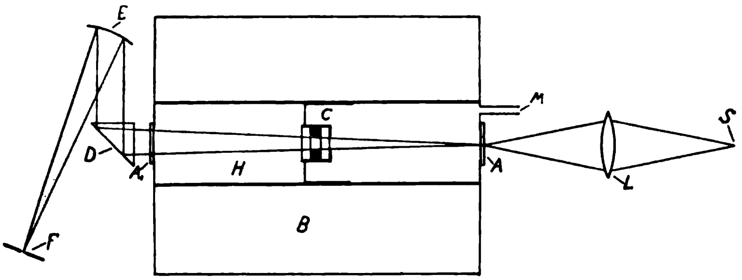


Fig. 1.

Source of Light.

A glass helium tube was used for wave-lengths between λ 6678 and λ 3188. For shorter wave-lengths this was replaced by a quartz mercury arc. It was found impossible to get interference bands with wavelengths below λ 2652 with the nickeled plates used. Photographs were taken with water-cooled arcs in a vacuum as the source of light. Cd, Zn, Cu, Bi, Al, Co, Ni, Fe, Ag, Sn, Al, and brass were tried, usually with the hotter electrode brass so that it would not melt during a long exposure. Cd, Zn, Cu, Al, Sn, and brass gave some good lines for longer wavelengths, Cd being the best, but there were no good lines below λ 2652. Therefore the idea of using a metallic arc in a vacuum was given up and the He tube and the Hg arc were used entirely.

PURITY OF GASES.

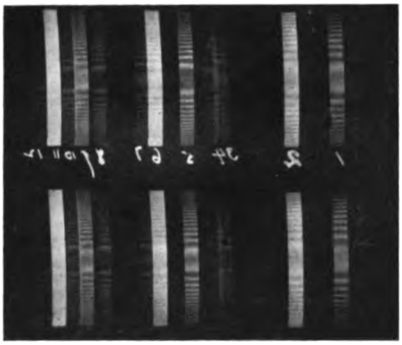
The gases used were air, oxygen, hydrogen and carbon dioxide. The oxygen was 98 per cent. to 99 per cent. pure, the hydrogen was prepared electrolytically and was 99.8 per cent. pure. Commercial carbon dioxide was used and its purity cannot be vouched for, but, as the dispersion curve found is almost identical with that of Rentschler, the purity of the gas is probably the same and the curve may be considered as an extension of his.

METHOD.

In calculating the index of refraction of any line the following procedure was used. Two exposures were taken on one plate, one at atmospheric pressure, the other with the pressure reduced almost to a vacuum. During the two exposures the temperature was kept constant. Before taking the photograph the number of whole bands going by for this change in pressure was counted for one of the visible lines. Knowing the number of whole bands going by for this line, the fraction was found in the following way:

In Fig. 2 we have the line λ 5876 at low and at atmospheric pressure. As the first two rings were always too broad to set on with accuracy, the diameters of the third to seventh rings were measured in both A and B, and, from the formula $D_2^2 - D_1^2 = (8R^2/P)$, the constant $(8R^2/P)$ was determined. D_1 and D_2 are the diameters of any two successive rings. P is the order of the ring system and R is the focal length of the concave mirror which focuses the ring system on the slit of the spectroscope. As P is of the order of magnitude of 25,000 and changes about 15 to 20 in going from the third ring at atmospheric to the seventh at low pressure, the error introduced by averaging the value of $(8R^2/P)$ from the diameters in both A and B is entirely negligible.

$$p = P_1 + P_1 \frac{x_1^2}{8}, \tag{1}$$



A Low Pressure.

B Atmospheric Pressure.

λ 5876

Fig. 2.

JANET TUCKER HOWELL.

where p is the order of interference at the center, P_1 is the order of the first ring, and x_1 is the angular diameter of the ring. Then the fraction of a ring that has passed the center is

$$p - P_1 = P_1 \frac{x_1^2}{8} = \frac{P_1 D_1^2}{8R^2}, \tag{2}$$

where R is the focal length of the mirror and D_1 is the diameter of the ring of order P_1. $(8R^2/P)$ is averaged for all the rings as described above. Then measuring the diameter of the third ring and substituting in (2) we get

$$p - P_3 = 2 + \text{a fraction}.$$

And, in the same way, for each diameter we get a whole number + a fraction, the fraction being the same for all rings of photograph B. In this way, the fraction is determined for atmospheric and then for low pressure, and the difference between these two fractions (atmospheric—low) will give the fraction of a band that has gone by for the change in pressure used. The whole number has been counted visually so that the whole number + the fraction $= k$, the total shift in interference bands for the known change in pressure.

Then

$$\mu - 1 = \frac{k\lambda}{2d} = \frac{k}{p}.$$

d is the distance in cm. between the interferometer plates; p is the order at the center; d and λ are known, so that p can be found, and, knowing p and k, we get $\mu - 1$, where μ is the index of refraction.

This having been done for one line in the visible spectrum, values can be found for the neighboring lines and in this way the readings may be extended into the ultra-violet. The fraction is found in the same way, and the whole number can be obtained from the whole number of the line above since, with this method, very few whole bands go by and, if six is the right number, five or seven will throw the values very far off the curve. The value of the result depends entirely on the accuracy with which the fraction is determined.

The values of $\mu - 1$ are reduced to standard conditions by means of the following equation

$$(\mu - 1)_{\text{standard}} = (\mu_1 - 1)\frac{76}{p_1}\left(1 + \frac{t_1}{273}\right).$$

p_1 is the difference in pressure used to calculate μ_1 and t_1 is the temperature of the bath during the exposure.

RESULTS.

The indices of refraction of the different gases investigated are given in Table I. at 0° C. and 76 cm. pressure. The dispersion curves are shown in Figs. 3 and 4. In Table I. the wave-length given as λ 3022 is a double line λ 3021 and λ 3023.

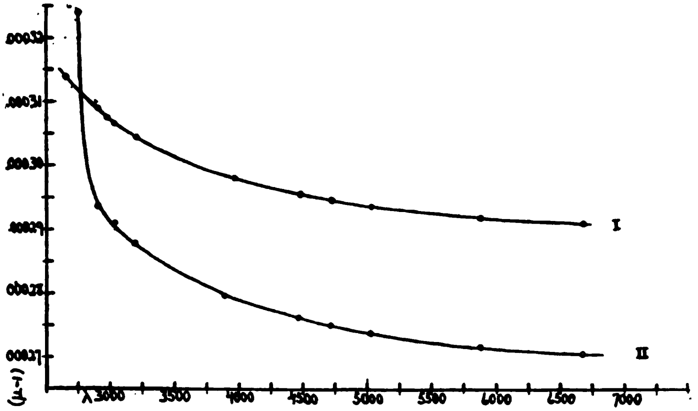


Fig. 3.

Dispersion Curves: I., Air; II., Oxygen. Abscissae: λ in Ångstrom units. Ordinates: $(\mu - 1)$.

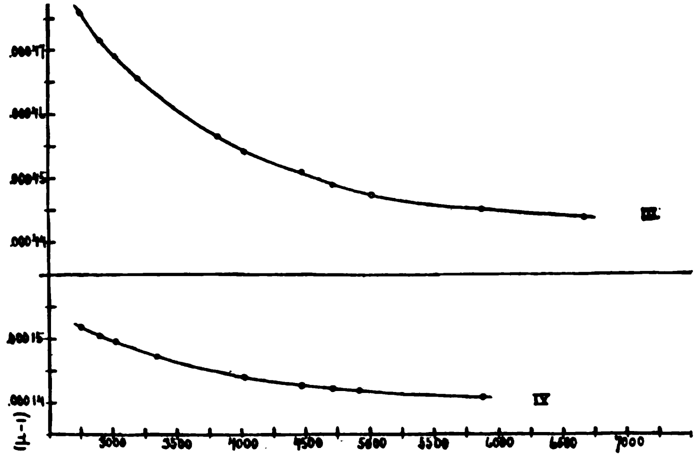


Fig. 4.

Dispersion Curves: III., Carbon Dioxide; IV., Hydrogen. Abscissæ: λ in Ångstrom units, Ordinates: $(\mu - 1)$.

DISPERSION FORMULÆ.

Air.

It has been customary to express dispersion curves in terms of the Cauchy formula

TABLE I.

λ in A. U.	Air (μ—1).	Oxygen (μ—1).	Hydrogen (μ—1).	CO_2 (μ—1).
6678 (He)	.00029120	.00027083		.00044379
5876 (He)	.00029196	.00027184	.00014105	.00044531
5016 (He)	.00029350	.00027401		.00044750
4916 (Hg)			.00014203	
4713 (He)	.00029440	.00027511	.00014238	.00044906
4471 (He)	.00029555	.00027631	.00014280	.00045119
4026 (He)			.00014440	.00045414
3965 (He)	.00029800			
3889 (He)		.00027965		
3820 (He)				.00045638
3341 (Hg)			.00014737	
3188 (He)	.00030430	.00028793		.00046549
3022 (Hg)	.00030662	.00029119	.00014973	.00046929
2967 (Hg)	.00030737			
2894 (Hg)	.00030902	.00029360	.00015061	.00047137
2753 (Hg)		.00032423	.00015187	.00047617
2652 (Hg)	.00031400			

$$\mu - 1 = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4},$$

although no theoretical importance can be attached to it. It is therefore given here so that the results can be compared with those of other observers.

Cuthbertson finds[1]

$$\mu - 1 = .00028854 + \frac{13.38}{\lambda^2\, 10^{16}} + \frac{5.0}{\lambda^4\, 10^{24}}.$$

Kayser and Runge give[2]

$$\mu - 1 = .00028787 + \frac{13.16}{\lambda^2\, 10^{16}} + \frac{3.16}{\lambda^4\, 10^{24}}.$$

Rentschler gives[3]

$$\mu - 1 = .0002903 + \frac{3.80}{\lambda^2\, 10^{16}} + \frac{1.23}{\lambda^4\, 10^{23}}.$$

As a result of this investigation the formula is found to be

$$\mu - 1 = .00028817 + \frac{11.83}{\lambda^2\, 10^{16}} + \frac{4.6}{\lambda^4\, 10^{24}},$$

which differs very little from the formula of Kayser and Runge.

The observed and calculated values are given below in Table II.

---

[1] Proc. Roy. Soc. (83), p. 151, 1909.

[2] Ann. d. Physik (50), p. 293, 1893.

[3] Astro. Jour. (28), p. 345, 1908.

TABLE II.

λ (A. U.).	$\mu-1$ (Obs.).	$\mu-1$ (Calc.).
6678	.00029120	.00029106
5876	.00029196	.00029198
5016	.00029350	.00029359
4713	.00029440	.00029444
4471	.00029555	.00029524
3965	.00029800	.00029756
3188	.00030430	.00030427
3022	.00030662	.00030663
2967	.00030737	.00030754
2894	.00030902	.00030884
2652	.00031400	.00031429

The mechanical theory of dispersion and the electrical theory for transparent media lead to the Sellmeier formula

$$\mu^2 - 1 = \Sigma \frac{D\lambda^2}{\lambda^2 - \lambda_m^2},$$

where D is a constant and λ_m is the wave-length of the free vibration of the electron. In the case of two absorption bands, one in the red and one in the violet, the formula takes the form

$$\mu^2 - 1 = \frac{D_v\lambda^2}{\lambda^2 - \lambda_v^2} + \frac{D_r\lambda^2}{\lambda^2 - \lambda_r^2}.$$

D_r is negative if $\lambda_r^2 > \lambda^2$. For the dispersion formula of air the values of D_v and λ_v^2 were found by using the values of the index of refraction of the wave-lengths λ 2894 and λ 2652, and substituting in

$$\mu^2 - 1 = \frac{D_v\lambda^2}{\lambda^2 - \lambda_v^2}.$$

$$D_v = 5.7 \times 10^{-4}.$$

$$\lambda_v^2 = .6455 \times 10^{-10}.$$

Using these constants and the values of μ for λ 6678 and λ 5876 and substituting in

$$\mu^2 - 1 = \frac{D_v\lambda^2}{\lambda^2 - \lambda_v^2} + \frac{D_r\lambda^2}{\lambda^2 - \lambda_r^2},$$

the two other constants were determined.

$$D_r = -8.067 \times 10^{-5}.$$

$$\lambda_r^2 = .10116 \times 10^{-6}.$$

So that the Sellmeier formula for air is found to be

$$\mu^2 - 1 = \frac{5.7\,\lambda^2\,10^{-4}}{\lambda^2 - .6455 \times 10^{-10}} - \frac{8.067\,\lambda^2\,10^{-5}}{\lambda^2 - .10116 \times 10^{-6}}.$$

The observed and calculated values of $\mu^2 - 1$ for the intermediate wave-lengths are given in Table III.

TABLE III.

λ (A. U.).	$\mu^2 - 1$ (Obs.).	$\mu^2 - 1$ (Sellmeier) Calc.	$\mu^2 - 1$ (Cauchy) Calc.
5016	.000 587 086	.000 587 053	.000 587 286
4713	.000 588 887	.000 588 860	.000 588 966
4471	.000 591 187	.000 590 931	.000 590 567
3965	.000 596 089	.000 595 676	.000 595 230
3188	.000 608 692	.000 609 460	.000 608 630
3022	.000 613 330	.000 613 160	.000 613 350
2967	.000 615 130	.000 615 770	.000 615 170

The agreement of the calculated with the observed values is about the same for the two formulæ. The Sellmeier formula is however the more interesting of the two on account of the theoretical value of the constants. The values of λ_v and λ_r for air cannot be taken to indicate definite absorption bands. They give the middle of regions of absorption in the red and violet, the absorption in the red being due probably to traces of water vapor.

Hydrogen.

It was found impossible to calculate the Sellmeier formula as there is no absorption band near enough to the region observed. The Cauchy formula found is

$$\mu - 1 = .000\ 138\ 76 + \frac{.8}{\lambda^2\, 10^{14}} + \frac{1.36}{\lambda^4\, 10^{24}}.$$

Cuthbertson gives[1]

$$\mu - 1 = .000\ 136\ 23 \left(1 + \frac{7.61}{\lambda^2\, 10^{11}}\right)$$

$$= .000\ 136\ 23 + \frac{1.0367}{\lambda^2\, 10^{14}}.$$

The calculated and observed values are given in Table IV.

It is possible, from the dispersion curve of hydrogen, to calculate the ratio of e/E, where e is the charge on the dispersion electron and E the charge on the hydrogen ion. Rutherford in his recent atomic theory has assumed that the hydrogen atom consists of a single electron and a nucleus with one + charge. Bohr[2] has found this theory successful in explaining the laws of spectral series for hydrogen and we may assume therefore that theoretically the ratio of e/E should equal unity.

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[1] Proc. Roy. Soc. (83), p. 151, 1909.

[2] Phil. Mag. (26), pp. 1, 476, 1913.

TABLE IV.

λ(A. U.)	($\mu - 1$) Obs.	($\mu - 1$) Calc.
5876	.000 141 05	.000 141 17
4916	.000 142 03	.000 142 30
4713	.000 142 38	.000 142 64
4471	.000 142 80	.000 143 10
4026	.000 144 40	.000 144 21
3341	.000 147 37	.000 147 02
3022	.000 149 73	.000 149 15
2894	.000 150 61	.000 150 25
2753	.000 151 87	.000 151 68

The method of calculating e/E is as follows. Assuming

$$\mu^2 - 1 = \frac{Ne^2}{\pi m(n_0^2 - n^2)}.$$

Then, since $\mu^2 - 1 = 2(\mu - 1)$ for gases

$$\mu - 1 = \frac{Ne^2}{2\pi m(n_0^2 - n^2)},$$

where N = no. of atoms in 1 c.c. of gas,

n = the frequency of the wave-length observed,

n_0 = the frequency of the free period of the electron,

m = the mass of the dispersion electron,

e = the charge on the dispersion electron.

Eliminating n_0^2 between two similar equations we get

$$\frac{Ne^2}{2\pi m}\left(\frac{1}{\mu_1 - 1} - \frac{1}{\mu_2 - 1}\right) = n_2^2 - n_1^2 = V^2\left[\left(\frac{1}{\lambda_2}\right)^2 - \left(\frac{1}{\lambda_1}\right)^2\right],$$

where V is the velocity of light. Therefore from two values of μ a value can be found for $Ne^2/2\pi m$. Then assuming $(e/m) = 5.1 \times 10^{17}$, we find Ne. By electrolysis

$$NE = 2.45 \times 10^{10},$$

where E = the charge on the hydrogen ion. Taking the ratio we find e/E, which theoretically should equal unity.

Campbell,[1] using Ketteler's values for the dispersion of hydrogen, found

$$\frac{e}{E} = .7.$$

Cuthbertson,[2] from his values, found

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[1] Modern Electrical Theory (1st edition), p. 90.

[2] Proc. Roy. Soc. (83), p. 151, 1909.

$$\frac{e}{E} = .85.$$

From the dispersion curve of hydrogen found in this work, the following values of e/E were calculated (Table V.).

Table V.

λ	$\frac{e}{E}$
2753–3022	1.08
2753–3341	.95
2753–4026	.93
2753–4916	.90
2753–5875	.92
2894–3341	.93
2894–4026	.92
2894–4916	.88
2894–5876	.91
3022–3341	.85
3341–4026	.91
3341–5876	.90
4026–5876	.90
4916–5876	1.14
	Mean = .94

This value of e/E shows that the assumption that the hydrogen atom consists of a single electron and a nucleus carrying one positive charge—an assumption that is so well justified by Bohr's work[1] on spectral series—is also justified by the dispersion curve of hydrogen.

Oxygen.

The oxygen dispersion curve rises so steeply in the ultra-violet that it was impossible to find constants in the Cauchy equation to fit the shor wave-length end of the curve. The following equation fits the curve in the region of longer wave-lengths.

$$\mu - 1 = .000\,2674 + \frac{1.2}{\lambda^2\,10^{14}} + \frac{1.06}{\lambda^4\,10^{23}}.$$

Cuthbertson[2] gives

$$\mu - 1 = .000\,265\,09\left(1 + \frac{7.33}{\lambda^2\,10^{11}}\right)$$

$$= .000\,265\,09 + \frac{1.943}{\lambda^2\,10^{14}}.$$

Rentschler gives[3]

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[1] Phil. Mag. (26), pp. 1, 476, 1913.

[2] Proc. Roy. Soc. (83), p. 151, 1909.

[3] Astro. Jour. (28), p. 345, 1908.

$$\mu - 1 = .000\ 269\ 74 + \frac{3.72}{\lambda^2\ 10^{15}} + \frac{1.26}{\lambda^4\ 10^{23}}.$$

It was found impossible to derive a satisfactory Sellmeier formula from the curve. Probably the reason for this is that the dispersion is influenced by too many absorption bands to be adequately represented by a formula of two terms. The observed values and those calculated from the Cauchy equation are given in Table VI.

TABLE VI.

λ (A. U.).	$(\mu-1)$ Obs.	$(\mu-1)$ Calc.
6678	.000 270 83	.000 270 62
5876	.000 271 84	.000 271 75
5016	.000 274 01	.000 273 80
4713	.000 275 11	.000 274 95
4471	.000 276 31	.000 276 05
3889	.000 279 65	.000 279 93
3188	.000 287 93	.000 289 48
3022	.000 291 19	.000 293 22
2894	.000 293 60	.000 296 81
2753	.000 324 23	.000 301 65

Carbon Dioxide.

The dispersion curve for carbon dioxide is very flat in the region investigated so that only the Cauchy formula was calculated. The formula found is

$$\mu - 1 = .000\ 4375 + \frac{2.58}{\lambda^2\ 10^{14}} + \frac{2.3}{\lambda^4\ 10^{24}}.$$

Rentschler[1] gives

$$\mu - 1 = .000\ 449\ 04 - \frac{16.55}{\lambda^2\ 10^{15}} + \frac{4.03}{\lambda^4\ 10^{24}}.$$

The observed and calculated values are as follows (Table VII.).

SUMMARY.

The result of this work has been to extend the dispersion curves of oxygen, hydrogen and carbon dioxide to λ 2753 and the dispersion curve of air to λ 2652. In regions previously investigated these curves agree well with those of other observers.

From the hydrogen curve the calculated value of e/E, the ratio of the charge on the electron to the charge on the ion, is found to be .94. This agrees remarkably well with the theoretical value 1 which follows from

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[1] Astro. Jour. (28), p. 345, 1908.

TABLE VII.

λ (A. U.).	(μ — 1) Obs.	(μ — 1) Calc.
6678	.000 443 79	.000 443 40
5876	.000 445 31	.000 445 16
5016	.000 447 50	.000 448 11
4713	.000 449 06	.000 449 58
4471	.000 451 19	.000 450 98
4026	.000 454 14	.000 454 29
3820	.000 456 38	.000 456 26
3188	.000 465 49	.000 465 32
3022	.000 469 29	.000 468 52
2894	.000 471 37	.000 471 58
2753	.000 476 17	.000 475 54

the assumptions on which the recent atomic theory of Rutherford is based. The method employed in this work is therefore found capable of very great accuracy for a small range of pressure change. Preliminary tests with large changes of pressure give indications of success in this direction although the large shift in interference bands may make it necessary to confine the work to the visible spectrum, where the whole number of bands going by can be counted.

In conclusion, I wish to thank Dr. James Barnes, at whose suggestion and under whose direction this investigation is being carried out, for the help and advice he has given me and the interest he has taken in the work.

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CHANGE OF PHASE UNDER PRESSURE.[1]

II. NEW MELTING CURVES WITH A GENERAL THERMODYNAMIC DISCUSSION OF MELTING.

BY P. W. BRIDGMAN.

THERMODYNAMIC SPECIFICATIONS OF THE MELTING CURVE.

The equation of the melting curve in terms of the characteristic equations of solid and liquid may be found as follows. In the following the subscript (1) will refer to the liquid, and (2) to the solid. It is to be noticed, however, that the analysis applies to any two different phases, whatever their nature. The same equations will be used again in discussing polymorphic transformations of solids.

We know that along the melting curve the thermodynamic potential Z, $(= E - tS + pv)$, is the same for the two phases, that is $Z_1 = Z_2$. If now, we know a single point on the melting curve, $(p_0 t_0)$, we can determine the equation of the curve. For we have

$$\left(\frac{\partial Z}{\partial p}\right)_\tau = v$$

and

$$\left(\frac{\partial Z}{\partial \tau}\right)_p = -S.$$

Hence if we know Z at A (see Fig. 21), we find Z at C by integrating $(\partial Z/\partial \tau)_p$ from A to B, and $(\partial Z/\partial p)_\tau$ from B to C.

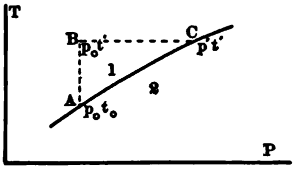

Fig. 21.

The paths followed in the integration for finding the difference of thermodynamic potential between liquid and solid.

Hence along AB,

$$Z(p_0 t') = Z_0 + \int_{\tau_0}^{\tau'} \left(\frac{\partial Z}{\partial \tau}\right)_p d\tau.$$

---

[1] Concluded from preceding number.

But

$$\left(\frac{\partial Z}{\partial \tau}\right)_p = -S = -\left[S_0 + \int \left(\frac{\partial S}{\partial \tau}\right)_p d\tau\right] = -\left[S_0 + C_p \log\frac{\tau}{\tau_0}\right].$$

This assumes that C_p is constant over the range in question. The equations are seen to give a good approximation, for variations of the first order in C_p produce variations of only the second order in Z. Substituting the values above and integrating gives:

$$Z(p_0\tau') = Z_0 - (S_0 - C_p)(\tau' - \tau_0) - C_p\tau' \log\frac{\tau'}{\tau_0}.$$

Similarly along BC we have

$$Z(p'\tau') = Z(p_0\tau') + \int_{p_0}^{p'} \left(\frac{\partial Z}{\partial p}\right)_\tau dp.$$

If now we abbreviate the thermal expansion, $(\partial v/\partial \tau)_p$, by β, and the compressibility, considered as positive, by α ($\alpha = -(\partial v/\partial p)_\tau$), we shall have,

$$\int_{p_0}^{p'} \left(\frac{\partial Z}{\partial p}\right)_\tau dp = \int_{p_0}^{p'} v\,dp = \int_{p_0}^{p'} [v_0 + \beta(\tau' - \tau_0) - \alpha(p - p_0)]dp$$

$$= (p' - p_0)\left[v_0 + \beta(\tau' - \tau_0) - \frac{\alpha}{2}(p' - p_0)\right],$$

and finally,

$$Z(p'\tau') = Z(p_0\tau_0) + (p' - p_0)\left[v_0 + \beta(\tau' - \tau_0) - \frac{\alpha}{2}(p' - p_0)\right]$$

$$- (S_0 - C_p)(\tau' - \tau_0) - C_p\tau' \log\frac{\tau'}{\tau_0}.$$

If now we insert the subscripts (1) and (2) to indicate liquid and solid, and put

$$Z_1(p'\tau') = Z_2(p'\tau'),$$

we have an equation for the melting curve. If we furthermore abbreviated $(\partial v_1/\partial \tau)_p - (\partial v_2/\partial \tau)_p$ by $\Delta\beta$, etc., the equation of the melting curve takes the form:

$$(p - p_0)[\Delta v + \Delta\beta(\tau - \tau_0) - \tfrac{1}{2}\Delta\alpha(p - p_0)] - (\Delta S_0 - \Delta C_p)(\tau - \tau_0)$$

$$- \Delta C_p\tau \log\frac{\tau}{\tau_0} = 0.$$

This equation holds only over a pressure range within which α, β, and C_p may be regarded as constant; this condition is not satisfied over the pressure range of this paper. In fact, it is the variations in $\Delta\alpha$, $\Delta\beta$, and ΔC_p that are of chief importance in determining the shape of the curve over any extended pressure range. This is suggested by what occurs in one simple case. If we assume that $\Delta C_p = 0$, the curve crosses the pressure axis twice, rising to a maximum temperature at some intervening pressure. But we have seen that this maximum temperature does not occur in nature. One important reason for this is that $\Delta\alpha$ does not remain constant, but liquid and solid approach each other in compressibility with rising pressure. In view of the large effect of the variations in $\Delta\alpha$, $\Delta\beta$, and ΔC_p along the melting curve, we will postpone discussion of the form of the curve determined by the above equation until we treat of polymorphic solids, because for solids we expect that these coefficients are more nearly constant than for liquids. The important problem before us at present is to determine as far as we can, the way in which $\Delta\alpha$, etc., vary along the melting curve. We shall indicate first what sort of data are needed for a determination of these quantities, and then get as much information as we can from the data at hand.

Although the equation of the melting curve does not hold over any extended pressure range, it does indicate the initial trend of things, and by differentiation can give us accurately the values of the first and second derivatives at the origin. The differentiation gives

$$\frac{d\tau}{dp} = \frac{\Delta v_0 + \Delta\beta_0(\tau - \tau_0) - \Delta\alpha_0(p - p_0)}{\Delta S_0 + \Delta C_{p0}\log(\tau/\tau_0) - \Delta\beta_0(p - p_0)}.$$

This evidently reduces to Clapeyron's equation, as it should, when $t - t_0$ and $p - p_0$ vanish, since

$$\Delta S_0 = \frac{\Delta H_0}{\tau}.$$

For the second derivative we get:

$$\frac{d^2\tau}{dp^2} = -\frac{1}{\Delta v}\frac{d\tau}{dp}\left[\frac{\Delta C_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\Delta\beta\frac{d\tau}{dp} + \Delta\alpha\right]. \qquad \text{(I)}$$

We see, therefore, that the curvature of the melting curve gives us one relation between the differences of compressibility, thermal expansion, and specific heat of solid and liquid. The melting curve we have seen to be always concave downwards, or $d^2\tau/dp^2 < 0$. This means, whether the curve rises like most curves, or falls like the ice curve, that

$$\frac{\Delta C_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\Delta\beta\frac{d\tau}{dp} + \Delta\alpha > 0.$$

If the curve should happen to be concave upwards, this would mean either an unusually small value of $\Delta\alpha$, or ΔC_p, or an unusually large value for $\Delta\beta$.

If the curve is to be accurately a straight line, with constant values of $\Delta\alpha$, $\Delta\beta$, and ΔC_p, then we must have the conditions satisfied: $\Delta C_p = 0$, and

$$\Delta\alpha = -2\Delta\beta\frac{d\tau}{dp}.$$

In addition to the information given by $d^2\tau/dp^2$, we may also obtain relations between $\Delta\alpha$, $\Delta\beta$, and ΔC_p from the curves for ΔV and ΔH. These relations may be easily deduced, and are

$$\frac{d\Delta H}{dp}=\frac{d\tau}{dp}\Delta C_p+\Delta v-\tau\Delta\beta, \qquad \text{(II)}$$

$$\frac{d\Delta V}{dp}=\frac{d\tau}{dp}\Delta\beta-\Delta\alpha. \qquad \text{(III)}$$

The quantities ΔV, $d\Delta H/dp$, and $d\Delta V/dp$ which enter these relations are to be determined from the curves already given. At first sight it appears that we now have three relations to determine $\Delta\alpha$, $\Delta\beta$ and ΔC_p, but as a matter of fact these relations are not independent. To see this, it is sufficient to observe that $\Delta\alpha$, $\Delta\beta$, and ΔC_p may all three be eliminated from I., II. and III., leaving the value of $d^2\tau/dp^2$ found by formal differentiation of Clapeyron's equation. Two of the relations are independent, however, so that we need only one more independent relation. The new relation must be experimental; we have exhausted the thermodynamic possibilities. At high pressures it might be possible to measure $\Delta\alpha$ or $\Delta\beta$ directly, but a direct measurement of ΔC_p would be much more difficult. Theoretically the measurements are already at hand to give $\Delta\alpha$; this could be determined from the difference of slopes of the isothermals above and below the melting point. But unfortunately very few of the curves are accurate enough to give useful information on this point. The difference of slope is small in any event, and the effect of a very minute quantity of impurity, producing a slightly premature melting, is sufficient in most cases to completely mask the effect sought. To find $\Delta\alpha$ directly, new experiments would be necessary. Perhaps the simplest way to do this would be to determine the isothermals of the solid at several temperatures considerably below the melting curve, and then extrapolate to the melting curve. This could be done without inaccuracy, because the variation of compressibility with temperature is small. Or a somewhat similar procedure would give $\Delta\beta$. However, two of the substances experimented upon give regular enough curves so that the directly determined values of $\Delta\alpha$ seem to have some significance. These quantities will be given later. Also we know from other experiments in a number of cases the values of $\Delta\beta$ or ΔC_p at atmospheric pressure. As complete a list as possible is given of these in the following.

Apparently the best we can do with this problem in general at high pressures is to try to get some idea of the magnitude of the quantities involved by approximations that seem reasonable. There are certain experimental inequalities that can help us. We have in the first place, the fact already mentioned, that universally $d^2\tau/dp^2 < 0$. We also have a nearly universal fact, for all the liquids so far worked with, that

$$\Delta v - \frac{d\Delta H}{dp} > 0$$

if $\Delta v > 0$. This condition may be readily proved to be equivalent in all cases to the condition

$$\frac{d}{d\tau}\left(\frac{\Delta H}{\tau}\right) < 0.$$

That is, the latent heat increases more slowly than the absolute temperature. This condition, if $d\tau/dp > 0$, is equivalent to

$$\frac{1}{\tau}\Delta C_p\frac{d\tau}{ap} - \Delta\beta < 0.$$

There are only two or three exceptional cases at isolated points for the eighteen liquids given above where $d\Delta H/d\tau$ has a very small positive value; the exceptions may be due to experimental error.

A third experimental inequality, with no exceptions, is that $d\Delta v/dp < 0$; that is, the change of volume decreases along the melting curve if positive, and increases in absolute value if negative. This inequality is equivalent to

$$\Delta\alpha > \frac{d\tau}{dp}\Delta\beta.$$

That is, along the melting curve the controlling factor in the change of volume is the difference of compressibility between the two phases, which is in general numerically greater and of opposite sign from the difference of thermal expansion along the melting line.

There is another universal feature of all the curves, namely that the Δv curve is concave upwards, or $d^2\Delta v/dp^2 > 0$. This condition, which is equivalent to

$$-\left(\frac{\partial\Delta\alpha}{\partial p}\right)_\tau + \left(\frac{d\tau}{dp}\right)^2\left(\frac{\partial\Delta\beta}{\partial\tau}\right)_p + \Delta\beta\frac{d^2\tau}{dp^2} > 0,$$

is of no immediate help to us here, because it gives the variations, instead of the actual values of $\Delta\alpha$ and $\Delta\beta$ along the curves.

In view of our inability at present to give precise values to $\Delta\alpha$, $\Delta\beta$, and ΔC_p, it becomes of interest to inquire if we cannot with the help of these inequalities find at least the order of magnitude of the several quantities. In general, we expect that $\Delta\alpha$, $\Delta\beta$, and ΔC_p are all positive, or that the compressibility, thermal expansion, and specific heat of the liquid are greater than the corresponding quantities for the solid. So far as I know, at atmospheric pressure, $\Delta\alpha$ is universally positive, even for water where the liquid occupies less bulk than the solid. $\Delta\beta$ is almost always positive; the only exception I know is for water, and even here $\Delta\beta$ becomes positive at higher pressures. And the only authentic example I know of a negative value for ΔC_p is that of sodium, recently measured by Griffiths.[34] We will assume in the following that these quantities are in general positive.

We rewrite the inequalities obtained so far

$$\Delta\alpha - \frac{d\tau}{dp}\Delta\beta > 0,$$

$$\frac{d\tau}{dp}\Delta\beta - \frac{1}{\tau}\Delta C_p\left(\frac{d\tau}{dp}\right)^2 > 0,$$

$$\frac{\Delta C_p}{\tau}\left(\frac{d\tau}{dp}\right)^2 - 2\frac{d\tau}{dp}\Delta\beta + \Delta\alpha > 0.$$

The terms entering these inequalities seem to be in general of the same order of magnitude, so that the inequalities usually can give us genuine information. As an average, for these experiments, $\Delta\alpha$ is of the order of 0.00001, $d\tau/dp$ of the order of 0.015, and τ of the order of 350°. This means that $\Delta\beta$ is of the order of 0.0006, and ΔC_p of the order of 10, or 0.2 cal. That is, $\Delta\alpha$, $\Delta\beta$ and ΔC_p are of the same orders as the compressibility, expansion, and specific heat of the liquid alone.

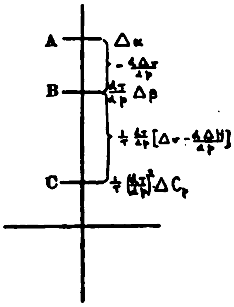
A
B
C
$\Delta\alpha$
$-\frac{d\Delta\tau}{dp}$
$\frac{d\tau}{dp}\Delta\beta$
$\frac{1}{\tau}\frac{d\tau}{dp}\left[\Delta v - \frac{d\Delta H}{dp}\right]$
$\frac{1}{\tau}\left(\frac{d\tau}{dp}\right)^2\Delta C_p$

Fig. 22.

Graphical representation of the relative magnitudes of the thermodynamic quantities determining the freezing curve. These relative magnitudes are determined by experiment.

The inequalities may be represented graphically, as shown in Fig. 22. The three quantities are arranged in descending order of magnitude, as shown. The experimental fact that $d^2\tau/dp^2 < 0$ is equivalent to the condition that the difference *A* to *B* is greater than the difference *B* to *C*.

The diagram makes clear what must happen in those exceptional cases when $\Delta\alpha$, $\Delta\beta$ and ΔC_p are not all positive. If $\Delta\alpha < 0$, solid more compressible than liquid, then we must also have $\Delta\beta < 0$, and $\Delta C_p < 0$. That is, $\Delta\alpha$ cannot be exceptional without all three being exceptional. Now if $\Delta\beta < 0$, we must also have $\Delta C_p < 0$, but there is no necessary condition as to sign thereby imposed on $\Delta\alpha$. Finally, if $\Delta C_p < 0$, there is no necessary condition of sign thereby imposed either on $\Delta\alpha$ or $\Delta\beta$. We may therefore say, since the normal state of affairs is for $\Delta\alpha$, $\Delta\beta$ and ΔC_p all to be positive, that the probability of negative values is greatest for ΔC_p, intermediate for $\Delta\beta$, and least for $\Delta\alpha$.

Besides these inequalities, the equations we have written down give us numerically the distances between A and B, and between B and C. Suppose now that we assume a probable value for one of the three quantities, and then compute the other two with the help of the known differences $A-B$ and $B-C$. It is obvious that we shall make the smallest percentage error in the other two if we assume ΔC_p, and the largest if we assume $\Delta\alpha$.

The numerical values that we give in the following will be computed in this way. We shall assume that $\Delta C_p = 0$, and then compute with the help of the above known differences the values of $\Delta\alpha$ and $\Delta\beta$. If, as is usually the case, ΔC_p is really positive, the values we find will be minimum values for $\Delta\alpha$ and $\Delta\beta$. The values for $\Delta\beta$ so found will not do much good, but the values for $\Delta\alpha$ will be somewhat better, and are perhaps worth giving. The values for all the eighteen liquids listed in this and previous papers will be computed in this way and tabulated.

In addition, where the results are available, the more accurate results will be given for atmospheric pressure. These accurate values at atmospheric pressure, combined with the rougher values at high pressures, will in some cases give us a better hold on the values under pressure. It should, however, be borne in mind that a direct experimental determination of either ΔC_p or $\Delta\beta$ is a matter of unusual difficulty, even at atmospheric pressure, because of the disturbing influence of premature melting due to very slight quantities of impurities. A striking example of the possibilities in this direction is shown in the discussion following under "sodium" of Griffiths' recent values. In particular, direct determinations of ΔC_p seem susceptible to error, as is shown by the very wide divergence of independent direct observations. In some cases, it is probable that the value of ΔC_p computed from the value of $\Delta\beta$ is better than the direct value. There seem to be practically no direct values of $\Delta\alpha$, either at atmospheric or higher pressures. In a few cases, I have, from my own data for determining ΔV at low pressures, been able to find a fairly good value for the difference of thermal expansion at atmospheric pressure, but in most cases the temperature range was not great enough to give satisfactory values for this.

DIFFERENCE OF COMPRESSIBILITY, EXPANSION AND SPECIFIC HEAT BETWEEN SOLID AND LIQUID.

In Table XI. are given these values of $\Delta\alpha$ at pressure intervals of 3,000 kgm. In addition, the values of $\Delta\beta$ at atmospheric pressure are listed. These values for $\Delta\beta$ should not be used without consulting the discussion, where the sources of information at atmospheric pressure are given and the most probable values indicated for each substance in detail.

TABLE XI.

Substance.	Difference of Compressibility (= $\Delta\alpha$).					Difference of Expansion (= $\Delta\beta$).	
	1	3,000	6,000	9,000	12,000	1	12,000
Potassium	$0.0_{5}47$	$0.0_{5}34$	$0.0_{5}27$	$0.0_{5}21$	$0.0_{5}16$	$0.0_{4}75$	?
Sodium	$0.0_{5}33$	$0.0_{5}18$	$0.0_{5}11$	$0.0_{6}8$	$0.0_{6}8$	$0.0_{4}89$	$0.0_{5}4$
Carbon dioxide		$0.0_{4}10$	$0.0_{5}9$	$0.0_{5}6$	$0.0_{5}35$		$0.0_{4}6$
Chloroform		$0.0_{5}37$	$0.0_{5}39$	$0.0_{5}30$	$0.0_{5}16$		$0.0_{4}4$
Anilin	$0.0_{5}82$	$0.0_{5}48$	$0.0_{5}36$	$0.0_{5}29$	$0.0_{5}30$	$0.0_{4}3$	$0.0_{4}8$
Nitrobenzol	$0.0_{4}11$	$0.0_{5}7$	$0.0_{5}32$	$0.0_{5}27$	$0.0_{5}24$[1]	$0.0_{3}11$	$0.0_{4}6$[1]
Diphenylamine	$0.0_{4}24$	$0.0_{5}7$	$0.0_{5}4$	$0.0_{5}3$[2]		$0.0_{3}28$	$0.0_{4}39$[2]
Benzol	$0.0_{4}50$	$0.0_{4}13$	$0.0_{5}6$	$0.0_{5}44$	$0.0_{5}38$[1]	$0.0_{3}48$	$0.0_{4}8$[1]
Carbon tetrachloride	$0.0_{4}12$	$0.0_{5}33$	$0.0_{5}33$	$0.0_{5}14$		$0.0_{3}12$	
O-Kresol { L- I	$0.0_{4}19$	$0.0_{5}8$	$0.0_{5}36$	$0.0_{5}21$		$0.0_{4}41$	
O-Kresol { L-II			$0.0_{5}30$	$0.0_{5}27$	$0.0_{5}14$		$0.0_{5}4$
Phosphorus	$0.0_{5}43$	$0.0_{5}28$	$0.0_{5}14$			$0.0_{3}10$	
Bromoform	$0.0_{5}49$	$0.0_{5}38$	$0.0_{5}28$	$0.0_{5}19$	$0.0_{5}16$[1]	$0.0_{4}46$	$0.0_{4}54$[1]
Silicon tetrachloride		$0.0_{5}87$	$0.0_{5}37$	$0.0_{5}17$	$0.0_{5}12$[1]		$0.0_{4}21$[1]
Chlorobenzol	$0.0_{4}11$	$0.0_{5}58$	$0.0_{5}36$	$0.0_{5}26$	$0.0_{5}15$	$0.0_{4}13$	$0.0_{4}4$
Bromobenzol	$0.0_{4}13$	$0.0_{5}49$	$0.0_{5}34$	$0.0_{5}17$	$0.0_{5}10$	$0.0_{3}21$	$0.0_{4}4$
Benzophenone	$0.0_{4}29$	$0.0_{4}13$	$0.0_{5}7$	$0.0_{5}3$[2]		$0.0_{3}47$	
p-nitrophenol	$0.0_{4}20$	$0.0_{4}16$[4]	$0.0_{4}12$[5]			$0.0_{3}11$	
p-toluidine	$0.0_{4}31$	$0.0_{4}13$	$0.0_{5}9$	$0.0_{5}7$[2]		$0.0_{3}44$	$0.0_{3}18$[2]
Methyl oxalate	$0.0_{4}67$	$0.0_{5}99$	$0.0_{5}6$	$0.0_{3}7$		$0.0_{3}41$	$0.0_{3}19$[3]
Bismuth	$0.0_{7}57$					$0.0_{4}8$	

[1] 11,000 kgm. [2] 8,000 kgm. [3] 9,000 kgm. [4] 2,000 kgm. [5] 4,000 kgm.

If there is no discussion for any substance, the value of $\Delta\beta$ was computed, assuming $\Delta C_p = 0$. The Table also gives in most cases, for purposes of orientation, the values of $\Delta\beta$ at 12,000 kgm., computed on the assumption that $\Delta C_p = 0$.

Potassium.—There are two experimental values for $\Delta\beta$ at atmospheric pressure; $0.0_{4}84$ by Block,[18] and $0.0_{4}64$ by Hagen.[52] If we assume as an average value $0.0_{4}75$, we find $\Delta\alpha = 0.0_{5}47$, and $\Delta C_p = 0.046$ cal. (1.95 kgm. cm./gm.). The difference of the specific heats found in this way is considerably less than either of two direct values that we have; 0.15 cal. by Bernini,[53] and 0.08 cal. by Joannis.[54] The probability seems to be that 0.046 is nearer the truth; the value of Bernini seems improbably large, and doubt is cast on the value of Joannis by the fact that his value for the latent heat is without doubt too high; as is suggested by the recent work of Griffiths[51] on a similar substance, sodium, for which Joannis' value is certainly too high.

The value found for $\Delta\beta$, assuming $\Delta C_p = 0$, is undoubtedly not good, for it is negative ($= -0.0_{4}25$), but the value for $\Delta\alpha$ on this assumption

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52. E. B. Hagen, Wied. Ann., *19*, 436–474, 1883.
53. A. Bernini, Nuov. Cim. (5), *10*, 5–13, 1905.
54. A. Joannis, Ann. Chim. et Phys. (6), *12*, 358, 1887.

is $0.0_{6}34$. We see, as was proved above, that $\Delta\alpha$ is not very sensitive to the value of ΔC_p. In the table, the value for $\Delta\alpha$ is assumed $0.0_{6}47$ at atmospheric pressure, and at 12,000 kgm. the value given is on the assumption that $\Delta C_p = 0$. At intermediate pressures, the initial difference of the two values $(0.0_{6}47 - 0.0_{6}34)$ is distributed proportionally to the pressure.

Sodium.—There are values for both ΔC_p and $\Delta\beta$ at atmospheric pressure. We have two values for ΔC_p, both negative; -0.07 cal. by Bernini,[53] and -0.06 by Griffiths.[51] Neither of these values are explicitly stated by the original authors, but have been estimated by me from curves plotted from their data giving C_p as a function of temperature above and below the melting point. In spite of the agreement of these values, careful examination of the data leaves the conviction that the agreement is accidental, and even leaves doubt as to whether the negative value for ΔC_p has been proved. The matter is of such importance that it will pay to dwell on it a little. In Fig. 23 are reproduced Griffiths' values for C_p above and below the melting point. It will be seen that the curve for C_p of the solid takes a sudden rise in the neighborhood of 70°. The question suggests itself whether this may not be due to a premature melting because of slight impurity. The amount of melting to account for this change of direction of the specific heat curve is very slight. If we suppose that the actual curve is really the dotted straight line, then the area between the dotted line and the curve through Griffiths' points represents the total heat set free in premature melting. This total heat is one fifth of a calorie which, combined with the latent heat, indicates that only two thirds per cent. of the total quantity of sodium need have melted prematurely to account for

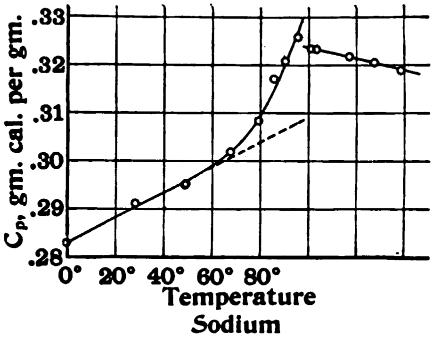

Fig. 23.

The recent values of Griffiths for the specific heat of solid and liquid sodium at atmospheric pressure. In the discussion it is pointed out that a very small quantity of impurity is sufficient to produce the deviation of the specific heat of the solid from linearity.

this. The total amount of impurity needed to produce this slight amount of melting is evidently much less than two thirds per cent., and may well be so small in amount as to resist most careful attempts to remove it. This consideration, of course, has been known for a long time to apply to determinations of differences of specific heat near the melting point, but this example of sodium shows in an unusually striking manner how very slight the amount of impurity need be in some cases to vitiate the result. It should be said that even if we assume the total variation of Griffiths' curve from linearity to be due to premature melting, the error so introduced into his value for the latent heat will be less than 1 per cent.

If we grant for the present the negative value for ΔC_p, and take the average of the two values, -0.065 cal. ($= -2.78$ kgm. cm.), we calculate $\Delta\beta = 0.0_424$. Now the value of $\Delta\beta$ determined by direct experiment is 0.0_483 by Block,[18] and 0.0_465 by Hagen.[52] These values are both considerably higher than that found by using the negative value for ΔC_p, and make improbable the validity of the negative value. If we compute backwards with the average of the two experimental values for $\Delta\beta$ ($= 0.0_474$) we shall find a very small negative value for ΔC_p, -0.0004 cal./gm. But it is to be noticed that the same causes which make ΔC_p appear negative will make the experimental values for $\Delta\beta$ too small, and it is significant that the later, and presumably more accurate value for $\Delta\beta$ is the larger. It seems to me that the safest course at present is to assume $\Delta C_p = 0$. This is the assumption made in getting the values of the table. It gives 0.0_489 for $\Delta\beta$, close to Block's value, and 0.0_533 for $\Delta\alpha$.

As this paper was going to press, I have come upon a recent paper by Rengade (C. R., *156*, 1897–1899, 1913), in which he finds that the specific heat of the liquid is greater than that of the solid by 0.045 cal. and the melting point of the pure metal is 97°.90. Beyond stating that great precautions were taken to obtain the metal especially pure, no detail is given.

Diphenylamine.—The experimental value for $\Delta\beta$ by Block,[18] 0.0_328, agrees well with the value computed above, 0.0_324, assuming $\Delta C_p = 0$. There are, however, two direct determinations of ΔC_p; 0.043 cal. by Batteli,[28] and 0.134 by Bogojawlensky.[55] The values of $\Delta\beta$ computed with these values of ΔC_p are 0.0_338 and 0.0_368 respectively. Both of these are considerably higher than the experimental values. Apparently Batteli's value for ΔC_p is much more nearly right than Bogojawlensky's. $\Delta\alpha$ is not appreciably changed by using Block's value for $\Delta\beta$ instead of 0.0_324.

Benzol.—The experimental value of Block,[18] 0.0_347, agrees unusually well with that found assuming $\Delta C_p = 0$, 0.0_346. The presumption is that ΔC_p is small. There are three widely varying experimental values for

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55. Bogojawlensky, quoted by Tammann in "K. und S.," p. 45.

ΔC_p; 0.131 cal./gm. by Ferche,[56] 0.003 by Fischer,[57] and 0.078 by Bogojawlensky.[55] If we assume the intermediate value, we find $\Delta\beta = 0.0_381$, which seems too much above the experimental value. Very recently, since the writing of most of this paper, Essex[58] has published data for the effect of pressure and temperature on the liquid and solid forms of benzol. His value for $\Delta\beta$ calculated by a linear extrapolation from his data for the solid at 1,500 and 2,500 kgm. is 0.0_350. There seems room for little doubt as to the approximate value of $\Delta\beta$ at atmospheric pressure.

Phosphorus.—There are three experimental values for $\Delta\beta$; 0.0_310 by Block,[18] 0.0_310 by Leduc,[59] and 0.0_465 by Kopp.[60] We shall assume the value 0.0_310. This is without doubt better than the value, which is 0, calculated assuming $\Delta C_p = 0$. If we assume 0.0_310 for $\Delta\beta$, we find $\Delta\alpha = 0.0_543$, against 0.0_514, calculated from $\Delta C_p = 0$. This is an exceptional case where $\Delta\alpha$ is sensitive to the value assumed for ΔC_p. In the table, the values of $\Delta\alpha$ are adjusted at high pressures as they were in the case of Potassium. The value of ΔC_p calculated assuming $\Delta\beta = 0.0_310$ is 0.027 cal./gm., which is in remarkably good agreement with the direct value, 0.026, found by Person.[61]

Monobrombenzol.—No direct experimental values are known for $\Delta\beta$ or ΔC_p, but this is the substance mentioned for which consistent experimental values of $\Delta\alpha$ were obtained over the pressure range. These values, at the pressure intervals of the above table, were 0.0_411, 0.0_56, 0.0_53, 0.0_51, 0.0_65, respectively. The agreement with the values computed assuming $\Delta C_p = 0$ is fairly good, and gives some confidence in the values for the other substances. It has been stated that the approximate values of the table are to be expected to be minimum values, but it will be noticed that the experimental values above are in most cases lower than the computed values. The reason for this is probably the unavoidable slight rounding of the corners of the freezing curve.

Benzophenone.—Block's[18] direct experimental value for $\Delta\beta$ is 0.0_347, against 0.0_319 assuming $\Delta C_p = 0$. There is no doubt that the direct value is better. The change in $\Delta\alpha$, however, is not so large; 0.0_429 using Block's value, and 0.0_421 assuming $\Delta C_p = 0$. The values at higher pressures are adjusted as in previous cases. Using 0.0_347 for $\Delta\beta$, we calculate $\Delta C_p = 0.075$ cal./gm., as compared with 0.096, the direct experimental value of Tammann.[62]

[56] J. Ferche, Wied. Ann., *44*, 265–287, 1891.

[57] W. Fischer, Wied. Ann., *28*, 400–432, 1886.

[58] H. Essex, Diss. Gött., 1914, Leopold Voss, Leipzig and Hamburg.

[59] A. Leduc, C. R., *113*, 259–261, 1891.

[60] H. Kopp, Trans. Roy. Soc., Vol. 155, 71–202, 1865.

[61] C. C. Person, Ann. Chim. et Phys. (3), *21*, 295–335, 1847.

[62] G. Tammann, "K. und S.," p. 240.

Paratoluidine.—For $\Delta\beta$ there is the direct value 0.0_330 by Block,[18] 0.0_322 calculated assuming $\Delta C_p = 0$, and 0.0_344, a direct value of my own. The range of values of $\Delta\alpha$, letting $\Delta\beta$ vary from 0.0_322 to 0.0_344, is only from 0.0_331 to 0.0_337, showing again the comparative insensitiveness of $\Delta\alpha$. The value of ΔC_p, using the extreme value of 0.0_344, is 0.068 cal./gm. This is considerably lower than 0.146, the only experimental value there is, by Batteli.[28] This is apparently much too high, because if we compute back to $\Delta\beta$, assuming 0.146, we find $\Delta\beta = 0.0_375$, which seems impossibly high. The value given in the table assumes $\Delta\beta = 0.0_344$.

Methyl Oxalate.—For $\Delta\beta$ at atmospheric pressure there is the value of Block,[18] who gives 0.000236. I find 0.000405. It is evident that the same impurity which invalidated Block's value for the change of volume will also affect the difference of expansion, and in the same direction as the difference between Block's value and mine. I have, therefore, used my own value in the computations. The values at the higher pressures have been calculated on the assumption that $\Delta C_p = 0$. It is to be remarked that, using my initial value for $\Delta\beta$, the initial value for ΔC_p is negative (− 15 kgm. cm.), an unusual and questionable result. This result depends on the large initial value for $d\Delta V/dp$ rather than on the value for $\Delta\beta$; it is quite probable that the initial value given above for $d\Delta V$ is really too large. There is a direct measurement of the difference of specific heats by Bruner,[34] who found that at the melting point the specific heat of the liquid was 1.41 kgm. m. greater than that of the solid. But Bruner's sample was unusually impure, as has been stated. In any event, this appears to be a substance for which the assumption that $\Delta C_p = 0$ is of more doubtful validity than usual.

Bismuth.—For this substance there are a number of data, none of which are very concordant, from which we may get some idea of $\Delta\alpha$, $\Delta\beta$ and ΔC_p at atmospheric pressure. For the specific heat of the solid there are the following values, shown in Table XII. A questionable extrapolation from all these values would indicate 0.0313 cal. as a probable value at the melting point. For the specific heat of the liquid there is only the value of Person,[42] 0.0363. The value of ΔC_p from these data is 0.0050 gm. cal. or 0.213 kgm. cm. per gm. For the thermal expansion there are two widely differing measurements. Vicentini and Omodei[43] find the average dilatation of the liquid between the melting point and 300° is 0.0_3120, the liquid increasing regularly in volume between these limits. Their value for the average expansion of the solid, presumably from room temperature up to the melting point, is 0.0_4395. Lüdeking,[47] on the other hand, finds that liquid bismuth has a maximum density at about 270°, just as water has above the freezing point. The freezing

TABLE XII.

C_p for Solid Bismuth.

Temperature.	C_p	Observer.	Temperature.	C_p	Observer.
−186°	.0284	Giebe[63]	50°	.03066	Lorenz[66]
− 79°	.0296	"	75°	.03090	"
18°	.0303	"	9°–102°	.02979	Bède[67]
17°– 99°	.0304	Voigt[64]	15°– 98°	.03084	Regnault[68]
22°–100°	.03035	Waterman[65]	20°–100°	.0314	Schüz[69]
0°	.03013	Lorenz[66]			

point he gives is about 260°. For the cubical expansion of the solid between 0° and 100° he gives 0.0_441. Lüdeking would make $\Delta\beta$ negative, therefore. His results seem open to considerable question, however, because he knew that there was some impurity of mercury, and because his melting point was 10° too low. If we assume that Vicentini and Omodei's value for $\Delta\beta$ is correct, and combine with the values that may be deduced from the above tables for $d\Delta V/dp$ (-0.0_78) and $d\Delta H/dp$, $(-0.0125$ kgm. cm.) we shall find for ΔC_p, 0.17 cal., against 0.21, the experimental value of Person. If, however, we assume the negative value for $\Delta\beta$ given by Lüdeking, we find 0.35 for ΔC_p. Vicentini and Omodei's values seem more probably accurate. The calculated value for $\Delta\alpha$ at atmospheric pressure, using Vicentini and Omodei's value for $\Delta\beta$, is -0.0_757. This means that the liquid, in spite of its smaller volume, is more compressible than the solid. If we combine this with the value for the compressibility given by Richards[70] for the solid at room temperature, 0.0_631 cm.^{3} per gm., we shall get some idea of the compressibility of liquid bismuth. At higher pressures, it turns out that bismuth is a substance for which the values of $\Delta\alpha$ are particularly sensitive to the values assumed for ΔC_p. If at atmospheric pressure we assume $\Delta C_p = 0$, we shall find for $\Delta\alpha$ 0.0_726 instead of 0.0_757. In view of this fact, it did not seem worth while to list the values of $\Delta\alpha$ at higher pressures assuming $\Delta C_p = 0$; one will find that on this assumption $\Delta\alpha$ becomes negative above 6,000 kgm., an improbable result.

Theorizing on the data of Table XI. can properly be left until more data are at hand. It will pay to emphasize, however, the fact that $\Delta\alpha$

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[63] E. Giebe, Verh. D. Phys. Ges.

[64] W. Voigt, Wied. Ann., Ann., *49*, 709–718, 1893.

[65] F. A. Waterman, PHYS. REV., Vol. 4, 161–190, 1896.

[66] L. Lorenz, Wied. Ann., *13*, 422–447, and 582–606, 1881.

[67] Bède, Mém. Acad. Roy. Belg., Vol. 27, 1855–56.

[68] V. Regnault, Ann. Chim. et Phys., 73, 1840.

[69] L. Schüz, Wied. Ann., *46*, 177–203, 1892.

[70] T. W. Richards, Pub. Carnegie Inst. Wash., May, 1907.

decreases very rapidly along the melting curve. We see that the equation written above for the melting curve in terms of $\Delta\alpha$ and $\Delta\beta$ cannot be expected to give even a rough approximation to the truth over so wide a pressure range as that here. It is also of interest to note that $\Delta\alpha$ approaches zero much more rapidly than does ΔV. This means that at high pressures the compressibility of liquid and solid are going to approach equality before the volumes reach equality. This seems to suggest that at high pressures a large part of the compressibility is afforded by the actual compression of the molecules, which would be expected to be the same for liquid and solid, while the outstanding difference of volume between liquid and solid is caused by the difference of structure. This observation comes to the same thing as a previous observation on mercury;[71] namely, that if the liquid should be compressed without freezing to the same volume as the solid, its compressibility would be less than that of the solid.

A comparison of the values of $\Delta\alpha$ and $\Delta\beta$ shows a state of affairs for the differences of compressibility and expansion similar to that previously found for the compressibility and expansion of liquids alone.[72] It was observed for liquids that the thermal expansion is decreased much less by pressure than the compressibility. An examination of the table and a comparison with the discussion of the numerical values shows that the decreases in the values of $\Delta\beta$ over the pressure range are much less than those for $\Delta\alpha$, in fact, for some of the substances the decrease is hardly noticeable.

A couple of other points in connection with the equation of the melting curve are worth especial comment. One is this; a complete thermodynamic knowledge of both liquid and solid separately is not enough to determine the location of the melting curve. It is well known that the behavior of a substance is completely determined thermodynamically if we can give the compressibility, thermal expansion, and specific heat at every point. Hence a complete thermodynamic description of solid and liquid separately determines the values of $\Delta\alpha$, $\Delta\beta$, and ΔC_p. But the equation of the melting curve contains one other quantity, ΔS, which cannot be found from the characteristic equation, but must be found by experiment. That is, we must find experimentally one point on the melting curve, and then the characteristic equation of solid and liquid will determine its course everywhere else. If, however, we knew the characteristic equation of the subcooled liquid down to $T = 0$, Nernst's equation would give a means of determining when $Z_1 = Z_2$.

The fact that the equation of the melting curve involves the thermodynamics of both liquid and solid has an important suggestion for the mechanism of melting. It means that melting is not determined by anything going on in the solid alone, or freezing by something in the liquid alone. For let us make the contrary hypothesis. We heat a solid at constant pressure, and let us suppose that when we arrive at a certain temperature the molecules of the solid become unstable and fall apart into the liquid. The contention is that this state of instability, whatever is the cause of it, cannot be determined by something taking place in the solid alone. For if we suppose for the moment that instability at the point under consideration is determined by the properties of the solid alone, we see, on heating the crystal again at a different pressure, that the new temperature of melting is determined by the properties of the liquid as well as those of the solid, and hence in general, the properties of both phases determine the melting point. Melting is not like the falling down of a row of dominoes. One possible explanation of this is that as a solid approaches the melting point, the molecules are in constant motion; some of them on the surface fall into the liquid, try it, and if the stability is greater there, the whole crystal follows; if the stability is less, they will ultimately recrystallize. This means that there may be something of the nature of balanced reactions at the melting point, the velocity of melting being equal to that of crystallization. A parallel case may make the nature of the reasoning here clearer. The angle of total internal reflection depends both on the index of refraction of the medium in which the reflection takes place, and on that of the surrounding medium. This means physically that the phenomena of reflection cannot be confined to the heavier medium, but some disturbance must penetrate into the lighter medium; that the light must try the second medium, as it were, and if it does not find it suitable, return to the first medium. This disturbance in the second medium is of course now known to exist, and may be accurately described.

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[71] P. W. Bridgman, Proc. Amer. Acad., Vol. 47, 423, 1911.

[72] P. W. Bridgman, Proc. Amer. Acad., Vol. 49, 1–114, 1913.

One special application of these considerations is that we are not justified in putting as the criterion of melting that the total expansion of the solid from the absolute zero shall reach a certain value, as is frequently done. For example, Lindemann's[73] deductions, by the aid of the quantum hypothesis and this special assumption, of the natural frequency of the atoms at the melting points, can at best be only an approximation.

THE HYPOTHESIS OF SCHAMES.

Very recently, Schames[74] has published a new hypothesis as to the nature of the equilibrium solid-liquid. This hypothesis is that there are two critical points between solid and liquid, one at $p = 0$, $\tau = 0$, and the other at $p = \infty$, $\tau = \tau_k$. That is, these two critical points lie on the boundaries of the region that can be reached; continuous passage from solid to liquid is not possible because we cannot go around the critical points. The hypothesis of a critical point at infinite pressure is equivalent to saying that the melting curve rises to a horizontal asymptote. It was the opinion of Schames that the critical temperature corresponding to infinite pressure was the same as the critical temperature liquid-vapor. This seemed to him to be indicated by a very wide extra-

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[73] F. A. Lindemann, Phys. ZS., *11*, 609–612, 1910.

[74] L. Schames, Verh. D. Phys. Ges., *15*, 1017–1026, 1913, and *16*, 518–528, 1914.

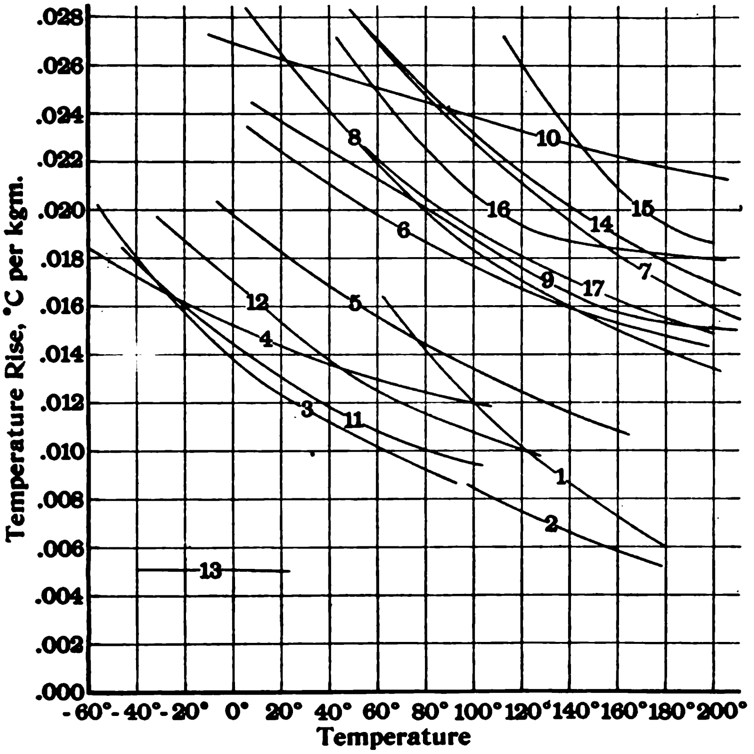

Fig. 24.

Collection in one diagram of the slope of the melting curves of most of the substances hitherto investigated in this series of papers, plotted against temperature. If the melting curve has a maximum temperature, the slope curve must cross the temperature axis vertically at a finite temperature; if it has a horizontal asymptote, it must cross the temperature axis at a finite angle at some finite temperature, or else it must become tangent to the axis at a finite temperature. The figures on the curves refer to the substances as follows: 1, potassium; 2, sodium; 3, carbon dioxide; 4, chloroform; 5, anilin; 6, nitrobenzol; 7, diphenylamine; 8, benzol; 9, bromoform; 10, silicon tetrachloride; 11, monochlorbenzol; 12, monobrombenzol; 13, mercury; 14, benzophenone; 15, paranitrophenol; 16, paratoluidin; 17, methyl oxalate.

polation from my data for water. This paper of Schames was published after the first of the present series of papers appeared, but was written before, so the data of the first paper were inaccessible to him. The fact, there stated, that the melting curve of CO_2 has been followed to above 100°, shows conclusively that the critical temperature, if it exists, cannot in general be the same as the critical temperature liquid-vapor. I have learned from private correspondence with Schames, however, that he does not regard this as an at all essential part of his theory; the essential point is the existence of the horizontal asymptote. It seems a matter of grave doubt, however, whether even this hypothesis is borne out by the data. In Fig. 24 the slope of the melting curve of a number of substances is plotted against temperature. If Schames's hypothesis is correct, these curves should tend to cross the temperature axis at a finite temperature. While one cannot say that the curves prove that this cannot be the case, it is nevertheless evident that such a state of affairs can be reached only by a very wide extrapolation, and that the curves, so far as known at present, offer no justification for supposing that there is such a critical temperature. The existence of curves like 16 shows that any extrapolation is hazardous, and in any event, it would seem to be the part of caution to be wary about extrapolating data from the comparatively low range of pressures open to direct experiment to " infinite " pressures. With out present conception of the structure of the atom, one may be prepared for entirely novel effects at pressures sufficiently high, even for the destruction of the atom itself.

THE EFFECT OF CHEMICAL CONSTITUTION.

There seem to be certain connections, not very definite, between the data of the melting curve and the chemical constitution. A number of these data are collected into Table XIII.: some substances are included here which will be more fully discussed in the next paper. In this table there are three groups of substances differing from each other only by the substitution of Br for Cl. These groups are CCl_4, CBr_4; $CHCl_3$, $CHBr_3$; and C_6H_5Cl, C_6H_5Br. We see that in every case replacing an atom of chlorine by a bromine has the effect of increasing $d\tau/dp$, Δv, and the melting point. There are two groups in the table in which an OH radical replaces a NH_2 radical, phenol, and anilin, and o-kresol and p-toluidine. The effect of the OH is to decrease both $d\tau/dp$ and Δv; the effect on the melting point is different in the two groups. Benzophenone differs from diphenylamine by the substitution of a NH group for a CO group. The heavier radical gives the larger $d\tau/dp$ and Δv. Similarly in the pair p-nitrophenol and o-kresol

Table XIII.

Chemical Relations.

Substance.	Formula.	Molecular Weight.	Melting Point.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$
Sodium	Na	23.05	97°.62	.02787	.00875
Phosphorus	P	31.0	44°.2	.01927	.0295
Potassium	K	39.10	62°.5	.02680	.0178
Carbon dioxide	CO_2	48.00	−56°.6	.14(?)	.0205
Benzol	C_6H_6	78.1	5°.43	.1317	.0286
Urethan	$CO\cdot NH_2\cdot OC_2H_5$	89.1	47°.90	.0599	.01105
Anilin	$C_6H_5NH_2$	93.1	− 6°.4	.0854	.0200
Phenol	C_6H_5OH	94.1	40°.87	.0567	.0140
p-toluidin	$C_6H_4\cdot CH_3\cdot NH_2$	107.1	43°.73	.1413	.0271
O-Kresol	$C_6H_4\cdot CH_3\cdot OH$	108.1	30°.8	.0838	.0177
Chlorobenzol	C_6H_5Cl	112.5	−45°.5	.072(?)	.0184
Methyl oxalate	$C_4H_6O_4$	118.0	54°.2	.1453	.0226
Chloroform	$CHCl_3$	119.4	−61 (?)	.065(?)	——
Nitrobenzol	$C_6H_5NO_2$	123.1	5°.6	.0814	.0219
p-nitrophenol	$C_6H_4\cdot NO_2\cdot OH$	139.1	114°	.0891	.0272
Carbon tetrachloride	$C\ Cl_4$	153.8	−22°.6	.0258	.0393
Bromobenzol	C_6H_5Br	157.0	−31°.1	.056?	.0191
Diphenylamine	$(C_6H_5)_2NH$	169.2	54°.0	.0958	.0257
Silicon tetrachloride	$Si\ Cl_4$	170.2	−67°.(?)	.052(?)	——
Benzophenone	$(C_6H_5)_2CO$	182.1	48°.11	.0904	.02845
Bismuth	Bi	208.5	271°.0	−.00345	−.00342
Bromoform	$CH\ Br_3$	252.9	7°.78	.0391	.0245
Carbon tetrabromide	$C\ Br_4$	331.8	92°		.062

in which a NO_2 replaces a CH_3, the heavier radical gives the larger $d\tau/dp$ and Δv. Nitrobenzol and anilin are another such group; the NO_2 of nitrobenzol replacing the NH_2 of anilin. In general, the effect of a heavier radical seems to be to increase both $d\tau/dp$ and Δv, with an irregular effect on the melting point. But in this respect the radicals H and OH are exceptional. The substitution of H for another radical may increase or decrease $d\tau/dp$ and Δv, and we have seen that OH decreases these quantities, although increasing the molecular weight. Other chemical similarities are not striking. In general, it seems that at present a discussion of the effects of chemical constitution is not very valuable, because the relations, if there are any, are not simple.

Summary.

The melting data for nine more substances have been obtained for the range from 0° to 200° and from atmospheric to 12,000 kgm. pressure. Bismuth has been investigated up to 270°. The evidence of these substances confirms the conclusion reached in the previous paper of this series; namely, that unless there is a reversal at high pressures of the effects found up to 12,000 kgm., the melting curve continues to rise with pressure and temperature indefinitely, with neither a maximum, nor a critical point.

The equation of the melting curve is obtained in terms of the difference of compressibility, thermal expansion, and specific heat between solid and liquid. It is shown that in virtue of certain experimental inequalities, we may obtain a fairly good approximation to the difference of compressibility between solid and liquid by assuming the difference of specific heats is zero. These approximate values of the difference of compressibility are given as a function of pressure for all the substances whose melting curves have been obtained hitherto. It is found that the liquid and solid approach each other in compressibility more rapidly than they do in volume. A discussion is also given, where the data are available, of the most probable values of the differences of thermal expansion and specific heat at atmospheric pressure. A suggestion as to the mechanism of melting is found in the fact that the equation of the melting curve involves the properties of both liquid and solid. Certain uniform effects of chemical constitution are found, but at present the chemical clue does not seem especially helpful.

In conclusion, it is a pleasure to acknowledge a generous grant from the Bache Fund of the National Academy, with which materials and mechanical assistance have been obtained.

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ON THE PRESENT THEORY OF MAGNETISM.

By Jakob Kunz.

THE electron theory seems to account for the magnetic phenomena in a very direct way. Indeed we have only to assume that the molecular currents of Ampere, which form the elementary magnets, are revolving electrons in order to express Ampere's theory of magnetism in terms of the electron theory. Nevertheless it was only on the basis of the researches of P. Curie that P. Langevin was able to account for the difference in diamagnetism and paramagnetism. Curie found that the diamagnetic susceptibility is independent of the temperature while the paramagnetic susceptibility is inversely proportional to the absolute temperature. Langevin concluded that there is a fundamental difference between diamagnetic and paramagnetic properties. In Langevin's theory the diamagnetism is a characteristic property of each atom which contains a certain number of revolving electrons. If the resultant magnetic moment of these electrons for an external point is zero, then the body is diamagnetic, the action of an external magnetic field consists in a change of the orbit, giving rise to the diamagnetic modification of the atom. If the revolving electrons possess a resultant magnetic moment, the body is paramagnetic. Matter in all its forms is diamagnetic; paramagnetism, whenever it appears, covers as it were the diamagnetism, and there is no transition between the two distinct groups. We shall add a short deduction of the diamagnetic susceptibility.

We consider in a diamagnetic gas an atom with an electronic orbit, of radius r, the electron e revolving with velocity v, in a plane perpendicular to the magnetic field. The moment will be equal to $M = \pi r^2(e/T)$ without magnetic field; if a field H is applied, the time of vibration T and the angular velocity will change, so that

$$dM = e\pi\left(\frac{2r}{T}dr - \frac{r^2}{T^2}dT\right),$$

or neglecting the first part

$$= - e\pi r^2\frac{dT}{T^2},$$

$$\frac{mv^2}{r} = f.r \text{ or } f = \frac{mv^2}{r^2},$$

$$\frac{mv^2}{r'} = fr' - \text{Hev}; \frac{mv^2}{r'^2} = f - \frac{\text{Hev}}{r'} = \frac{mv^2}{r^2} - \frac{\text{Hev}}{r'},$$

$$\frac{mv^2}{r'^2} - \frac{mv^2}{r^2} = \frac{\text{Hev}}{r'},$$

$$m2\pi\left[\frac{1}{T'^2} - \frac{1}{T^2}\right] = \frac{He}{T'},$$

$$m4\pi\frac{dT}{T^2} = He; \frac{dT}{T^2} = \frac{He}{4\pi m},$$

$$dM = \frac{-e^2r^2}{4m}H.$$

If there are N orbits per unit volume and if the axes are uniformly distributed in all directions, then we have

$$M = -\frac{e^2r^2N}{12m}H, \text{ or } k = -\frac{e^2r^2N}{12m}.$$

Apparently N and r are independent of the temperature. This theory of Langevin of the diamagnetic susceptibility k is at the same time the theory of the Zeeman effect.

In order to find the expression for the paramagnetic susceptibility fo a gas, we shall use a method quite different from that of Langevin. Let the angle between an external magnetic field H and the direction of the moment M of an elementary magnet be equal to α, the work required in order to rotate the magnetic particle from the direction H into its present direction will be equal to $W = -MH\cos\alpha + C$; the heat of the gas will change by this amount, and in order to keep the temperature constant, we have to add a quantity of heat $Q = -W = MH\cos\alpha$, and the increase of entropy will be equal to $S = (Q/T) = (MH\cos\alpha/T)$; and this entropy will be proportional to the lograithm of the probability P that we find the magnet in the direction α

$$S = R\log P + \text{const.} = \frac{MH\cos\alpha}{T},$$

$$P = e\frac{MH\cos\alpha}{RT},$$

and the number of magnets which are found in an angular interval $d\alpha$ will be proportional to P, or

$$dn = Ke\frac{MH\cos\alpha}{RT}\cdot d\omega,$$

where

$$d\omega = 2\pi \sin \alpha \, d\alpha,$$

$$dn = Ke^{\frac{MH \cos \alpha}{RT}} 2\pi \sin \alpha \, d\alpha,$$

the total number N of molecules per unit volume will be

$$N = 2\pi K \int_a^\pi e^{a \cos \alpha} \sin \alpha \, d\alpha,$$

where we put a for (MH/RT),

$$N = \frac{4\pi K}{a} \sin ha$$

and the intensity of magnetization $\mathfrak{J}$ becomes:

$$\mathfrak{J} = \int_0^\pi M \cos \alpha \, dw$$

$$= MN\left(\frac{\cos ha}{\sin ha} - \frac{1}{a}\right).$$

The maximum value of the intensity of magnetization $\mathfrak{J}_m = MN$, hence

$$\mathfrak{J} = \mathfrak{J}_m\left(\frac{\cos ha}{\sin ha} - \frac{1}{a}\right) = \mathfrak{J}_m\left(\frac{1}{3}a - \frac{2}{90}a^3 + \frac{4}{45{\cdot}42}a^5 - \dots\right).$$

Neglecting the higher powers of $a = MH/RT$ we find

$$\mathfrak{J} = \mathfrak{J}_m \frac{MH}{3RT} = kH,$$

$$k = \frac{NM^2}{3RT},$$

that is, the paramagnetic susceptibility is inversely proportional to the absolute temperature; that is the rule of Curie.

Experimental Facts.

The phenomena are far more complicated than the theory of Langevin indicates. The investigations of H. DuBois, K. Honda, M. Owen, Kamerlingh Onnes, P. Weiss, A. Perrier and others have revealed a very large variety of phenomena, in which the rules of Curie are altogether exceptions so that we have to extend or abandon the present theories.

The diamagnetic susceptibility should be an atomic property, which is independent of temperature, of a change of state, of a polymorphic transformation or of chemical combination. This is not the case. For instance, the diamagnetic susceptibility of amorphous carbon, of Cu, Zn, Zr, Cd, $\mathfrak{J}$n, Sb, Te, Tl, $\mathfrak{J}$, Pb, Bi, decreases with increasing temperature, k in the melting of Ag, Sn, Sb, Ga, Ge, Au, Hg, Tl, Pb, Bi changes discontinuously. In the polymorphic transformation of C, S, Sn, and Tl the susceptibility changes abruptly, even the sign changes in the polymorphic transformation and during the melting process of tin. In the case of boron (0–400° C.), diamond, silver and iodine (0–114°) the diamagnetic susceptibility increases with the temperature. There are only a few elements whose diamagnetic *k* remains constant within a certain interval of temperature; the diamagnetic susceptibility of an inorganic compound is not an additive property. Oxygen, for instance, is a strongly paramagnetic element, but if it combines with the paramagnetic elements of Be, Mg, Al, Mo, W, Th, it forms diamagnetic oxides. And in general the diamagnetic and paramagnetic properties depend so much on physical and chemical influences, that one might be inclined to ascribe them to electrons which are revolving on the surface of the atom. In organic compounds, at all events, it has been shown by P. Pascal that the molecular susceptibility X is an additive property of the atomic susceptibility. Oxygen in these compounds may be para- or diamagnetic. In more complicated compounds, the structure has a great influence on X. The diamagnetic constants are on the whole not smaller than the positive paramagnetic values.

The diamagnetic susceptibility of graphite is greater than the paramagnetic susceptibility of such an element as manganese, one of the strongest paramagnetic elements; charcoal, bismuth and antimony have also large negative susceptibilities. Besides in the crystals of graphite and antimony *k* varies with the direction of the axes. All these facts seem to indicate that what we observe is the difference between a positive and negative magnetism.

A similar variety of phenomena is observed in paramagnetism. Oxygen follows Curie's law at ordinary and at higher temperatures, but at lower temperatures the susceptibility varies inversely as the square root of the absolute temperature and finally probably becomes constant. Over certain intervals of temperature the susceptibility remains constant in the elements: Na, Al, K, V, Cr, Nb, W, Os, and even increases with increasing temperature in the case of Ti, V, Cr, Mn, Mo, Ru, Rh, 𝔍r, Th. The ferromagnetic metals above the critical temperature, where the ferromagnetism disappears, seem to follow Curie's law, probably with the exceptions of the compounds Fe_3O_4 and pyrrhotite.

An extension of Langevin's theory is necessary both for the diamagnetic and the paramagnetic susceptibility. In the first place, in Langevin's theory it is silently assumed that the moments of the elementary magnets are independent of the temperature. This assumption is by no means self-evident. The electrons revolve in the outer layers of the atoms probably and the moment of a molecule is the resultant of the moments of the atoms. With increasing temperature we have reasons to believe, the atoms share the energy of temperature agitation and the resultant moment of the molecule may be affected. Besides the fact that the diamagnetic susceptibility changes abruptly, in polymorphic transformations, in changes of state, in chemical transformations, indicates, that the diamagnetism is not simply an additive atomic property. In general we have to put:

$$M = M_0 f(T).$$

In the second place Langevin's theory of paramagnetism applies only to gases and dilute solutions. The resultant magnetic moment per unit volume depends only on the directing power of the field and on the "scattering" power of the temperature agitation. The equilibrium between these two effects leads to Curie's rule. But as soon as we consider a more condensed state of aggregation, the molecules will exert an influence on each other, and this influence for crystals will vary in different directions. P. Weiss has indeed extended Langevin's theory to ferromagnetic substances by adding to the external field H an internal or molecular field $N\mathfrak{J}$ which is proportional to the intensity $\mathfrak{J}$ of magnetization. In this way P. Weiss was able to explain a large number of phenomena of ferromagnetic crystals. A similar influence however must exist in paramagnetic solid and liquid substances. The mutual action of the molecules will be a certain function of the temperature $f(T)$ and will in general oppose the tendency of the external field to direct the elementary magnets, just as the temperature agitation; so that the energy of the opposing forces may be written in the form; $RT + f_1(T)$; the parameter a will now be equal to $\frac{M_0 f(T) H}{RT + f_1(T)}$ and $\mathfrak{J}$ will become:

$$\mathfrak{J} = M_0 f(T) N \left[\frac{\cos ha}{\sin ha} - \frac{1}{a}\right]$$

$$\mathfrak{J} = M_0 f(T) N \left[\frac{1}{3}a - \frac{2}{90}a^3 + \dots\right]$$

or approximately:

$$\mathfrak{J} = [M_0 \cdot f(T)]^2 \frac{HN}{3[RT + f_1(T)]},$$

$$k = \frac{[M_0 f(T)]^2 N}{3[RT + f_1(T)]}.$$

if $f(T)$ is a constant, for instance, equal to 1 and $f_1(T)$ also a constant ΘR, then we find

$$k = \frac{M_0^2 N}{3(RT + \Theta R)}$$

or

$$k(T + \Theta) = \text{constant},$$

a result which has been deduced by E. Oosterhuis[1] from Planck's theory of quanta of energy by entirely different considerations. At very low temperatures the specific heat of all substances seems to approach zero, the coefficient of expansion approaches zero also, the electrical conductivity of metals becomes very large, if not infinite, the thermal conductivity increases rapidly. All these properties can be explained by the assumption that at these very low temperatures in the neighborhood of the absolute zero the molecules gradually lose their mobility, and a given substance at absolute zero is a real solid body, as it were one large molecule, where the molecular mobility has disappeared; that means that the influence of the temperature agitation of the individual elementary magnets becomes weaker and weaker and that we can not even define the molecular magnet, because the whole system of magnets is as it were solidified, so that even at the absolute zero saturation of a substance is impossible and that the influence of temperature becomes smaller and smaller or the paramagnetic susceptibility becomes constant. This seems to be the tendency of solid oxygen.

If now at the lowest temperatures the function $([f(T)]^2/RT + f_1(T))$ is a constant, and at rather high temperatures is equal to $1/T$ and changes continuously from one extreme to the other, then it will in intermediate temperatures be approximately equal to $1/T^{\frac{1}{2}}$, and for this interval we shall have:

$$k = \frac{M_0^2 N}{3T^{\frac{1}{2}}},$$

a result which has been obtained by H. Kamerlingh Onnes and A. Perrier for liquid and solid oxygen. The formula $k(T + \Theta) = C$ or $X(T + \Theta) = C$, where X is the molecular susceptibility will be tested by means of measurements made in Leiden[2] on manganese sulfate.

In the next place the free electrons will be considered as contributing to the diamagnetic susceptibility. It has been shown by H. E. Dubois and K. Honda that the diamagnetic susceptibility of amorphous carbon, Cu, Zn, Cd, In, ℑ, Sb, Te, Tb, Pb, Bi, Sb decreases with increasing temperatures. The strongest diamagnetic metals are Sb and Bi, which show also a very large Hall effect. The magnetic field seems to act on

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[1] Die Abweichungen vom Curie'schen Gesetz im Zusammenhang mit der Nullpunktsenergie. Phys. Zeitschrift, Vol. XIV., p. 862, 1913.

[2] Leiden, Comm. No. 132e.

$M_nSO_4H_2O$				M_nSO_4			
$T_{abs.}$	$X \cdot 10^6$ Abs.	$C 10^{10}$	$\Theta = 1.18$	$T_{abs.}$	$X \cdot 10^6$	$C 10^{10}$	$\Theta = 26.5$
288.7	66.3	1.92		293.9	82.8	2.82	
169.6	111.5	1.905		169.6	144.2	2.83	
77.4	247	1.93		77.4	274.8	2.85	
70.5	270	1.93		64.9	314.5	2.87	
64.9	292	1.93		20.1	603	2.82	
20.1	914	1.94		17.8	627	2.78	
17.8	1,021	1.94		14.4	636	2.60	
14.4	1,233	1.92					

the free electrons so that they move in spirals or circles and produce diamagnetism. E. Schrödinger[1] found for the contribution k of the diamagnetism, made by the free electrons:

$$k = -\frac{1}{3}\frac{e^2}{m}\lambda^2 N,$$

where N is the number of free electrons per unit volume, and λ the mean free path. The effect, calculated in this way, is 100 times too large for silver and copper, which seems to be another argument against the "free" electrons in metals. Nevertheless the action of temperature on diamagnetism and the fact that Sb and Bi have a large Hall effect and a large negative magnetism indicate that the conduction electrons contribute somewhat to the diamagnetism.

THE PERIODIC SYSTEM OF THE ELEMENTS AND THEIR MAGNETIC PROPERTIES.

The elements may be arranged in series according to the atomic weights in different ways. A certain periodicity between atomic weights and magnetic properties always appears. If the atomic weights are represented by abscissæ and the magnetic susceptibilities as ordinates, the curve obtained is of a most irregular character, representing seven distinct maxima, among which that of the iron group is by far predominating. If only the sign of the magnetic properties is taken into account, one gets the best representation perhaps by the method of the helix due to B. K. Emerson, which is given in Fig. 1.

The strongly magnetic groups appear on a diameter, where we find Fe, Ni, Co, then Pd, Ru, Rh, then Gd, En, Sm, then Pt, Ir, Os. Moving on the spiral from iron to the right, we meet Mn and Cr, elements which are paramagnetic, but whose strongly magnetic properties appear only in some of their alloys and compounds such as the Heusler alloys, manganese-antimony, manganese-tin, manganese-zinc, Cr_5O_9. On the right hand side from the ferromagnetic elements, there are paramagnetic elements, on the left hand side the diamagnetic elements. Opposite to the magnetic metals there are the inert gases, which seem to be weakly diamagnetic. On the right-hand side of the inert gases we find the alkali metals whose weakly paramagnetic properties are not yet sufficiently known. The strongly magnetic metals, cobalt, nickel and iron, belong to the elements with minimum compressibility, with most complex

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[1] Kinetische Theorie des Magnetismus, Sitz. Ber. der K. Akademie der Wissenschaften, IIa, Bd CXXI., p. 1305, 1912.

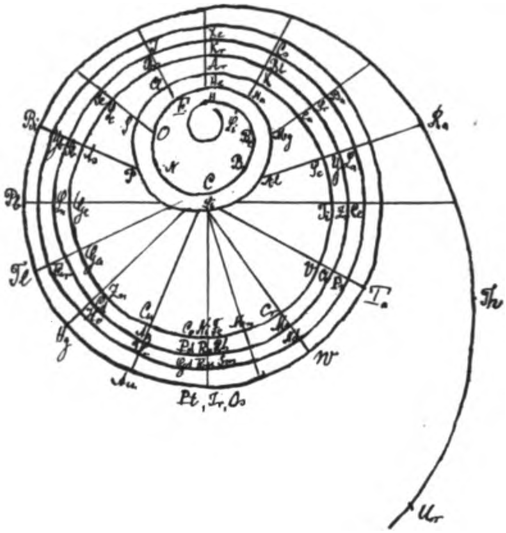

Fig. 1.

spectra, with complex double salts, with great condensation of mass, the heavy metals. Thus it looks as if condensation of electronic orbits were a maximum in these ferromagnetic metals and that the magnetic properties were related directly or indirectly to the mechanical, optical and chemical properties. It is very remarkable that immediately after the strongly magnetic metals there follow the diamagnetic metals:

	k
Cu	−0.66
Ag	−1.4
Tb	
Au	−2.6

On the next diameter we have:

Zn	−0.96
Cd	−1.16
Ho	
Hg	−2.6

When we move outward on a diameter of the spiral, the diamagnetic susceptibility increases. The same rule is repeated by chlorine, bromine and iodine; sulphur, selenium and tellurium; phosphorus, arsenic, antimony, bismuth. If a represents the atomic weight, α and β two constants, then the atomic susceptibility can be represented for the last three groups by

$$X_a = - C_e^{+\beta a - \alpha}.$$

The same law seems to hold for all the groups of diamagnetic elements which are in the previous representation on the left of the diameter passing through the iron group and the inert gases. Thus, for instance, for zinc, cadmium and mercury we find:

$$X_{zn} = \frac{0.96 \cdot 65.4}{7.1} 10^{-6} = 8.83 \cdot 10^{-6},$$

$$X_{Cd} = \frac{1.16 \cdot 112.4}{8.6} 10^{-6} = 15.2 \cdot 10^{-6},$$

$$X_{Hg} = \frac{2.6 \cdot 200}{13.6} 10^{-6} = 38.3 \cdot 10^{-6}.$$

If we put

$$x_a = 10^{\beta . a + \alpha}$$

we find from Cd and Hg for α and β the values:

$$\alpha = 0.6146, \ \beta = 0.00502,$$

log X_{zn} = 1.583, the calculated value = 1.618.

The agreement is not so good for the last diamagnetic group of elements: Cu, Ag and Au, here the atomic susceptibilities are as follows:

$$X_{cu} = 5.29 \cdot 10^{-6},$$

$$X_{Ag} = 14.39 \cdot 10^{-6},$$

$$X_{Au} = 26.55 \cdot 10^{-6}.$$

The copper seems to make an exception. Whether this is due to an inaccurate determination of X or to the fact that this element follows immediately after the iron group, remains an open question. Between the Zn, Cd, Hg group and the P, As, Sb group there are two more groups of diamagnetic elements, namely, those of Ga, 𝔍n, Tl and Ge, Sn, Pb. The few values of X known for these elements show that this magnetic constant increases toward the periphery along the diamagnetic diameter of the spiral.

If we travel along the spiral from copper towards zinc and from silver toward cadmium, we find the following values for the atomic susceptibilities.

Cu	$5.29 \cdot 10^{-6}$	Ag	$14.4 \cdot 10^{-6}$
Zn	8.83	Cd	15.2
Ga		𝔍n	
Ge		Sn	5.95
As	5.8	Sb	77.5
Se	24.0	Te	38.9
Br	21.9	𝔍	46.5

With the exceptions of As and Sn the atomic susceptibility increases from the south toward the north of the graphic representation. While in the strongly magnetic metals the susceptibility decreases as we move on the diameter outward, the diamagnetic susceptibility increases when we travel in the same direction. Oxygen occupies an exceptional position through its paramagnetic properties. Its regular diamagnetic properties appear only in some of the organic and inorganic compounds.

No theory of magnetism is complete, which is unable to account for the exceptionally high magnetic constants of iron, nickel and cobalt and of the other few ferromagnetic substances like the Heusler alloys. All elements can be divided into an electropositive and an electronegative group; all elements are either para- or diamagnetic. Just as we can try to ascribe the forces of affinity to electrical charges in the atom, we might try to reduce affinity to magnetic forces, or magnetons. It is very interesting to note that the strongest positive metals of the alkali group are the weakest paramagnetic elements; and that the most negative elements like F, Cl, Br, 𝔍, are rather strongly diamagnetic. While the chemical properties of the most electropositive and electronegative elements may be explained by electrical forces, it seems possible to think that the magnetic forces due to magnetic doublets play a similar rôle in the chemical affinity of the elements with strongly magnetic properties. In this way we should get a periodicity of the magnetic properties as functions of the atomic weight as we have a periodic variation of the electropositive and negative properties of the elements. The graphical presentation of the law of periodicity shows the strongly magnetic metals just opposite to the strongly positive and negative metals. This explanation of the periodic variation of the magnetic properties would obtain strong support if it were possible to prove that all magnetons are identical just as all electrons are identical. But there is very little evidence in favor of the identical nature of all magnetons or elementary magnets as we shall see in the last paragraph. In three investigations[1] published in this journal the moments of the elementary magnets and the charge *e* have been determined for the following substances.

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[1] The Absolute Values of the Moments of the Elementary Magnets of Iron, Nickel, and Magnetite, PHYSICAL REVIEW, Vol. XXX., p. 359, 1910. Stifler, PHYSICAL REVIEW, Vol. XXXIII., p. 268, 1911. P. Gumaer, PHYSICAL REVIEW, Vol. XXXV., p. 288, 1912.

	$m 10^{20}$	$e \cdot 10^{20}$
Fe	5.15	1.60
Fe_3O_4	2.02	0.90
Ni	3.65	1.54
Co	6.21	1.56
Heusler alloy 1	3.55	1.54
Heusler alloy 2	4.23	2.04

$1.53 \cdot 10^{-20} = e$ (average).

This value of e agrees fairly well with the values obtained by independent methods. On account of the necessary extrapolations it is difficult to obtain higher accuracy.

While I used the Langevin-Weiss theory for the determination of the elementary moment m, P. Weiss himself measured the intensities of magnetization at very low temperatures, and found noticeable deviations between the theory and the experiment in the temperature-intensity curve and he found at the same time a common divisor among the molecular intensities of the ferromagnetic substances. He called that divisor the magneton-gram, for which he gave the value 1,123.5. In addition the paramagnetic susceptibility of Fe_3O_4 above the critical temperature showed discontinuities as function of the temperature, which consisted of four straight lines, each of which led to a new determination of the magneton. Finally P. Weiss applied the equation

$$C_m = X_m T = \frac{\sigma_{m0}^2}{3r}$$

to solutions of paramagnetic substances containing iron and to a considerable number of solid salts. It has been shown, however, by Koenigsberger and Meslin that the molecular coefficient of magnetization of dissolved substances is a function of the concentration; at least for some solutions, while for others it seems to be constant. This fact makes it necessary to study solutions infinitely dilute or undissolved substances. The number of magnetons found by Weiss in the various substances is shown by the following series, in which the values coincide nearly with whole numbers.

10.41
21.89
21.96
24.04
28.03
27.93
30.09
25.99
27.11
27.91
27.69

28.83
26.99
28.94
29.19
21.23
25.05
17.97
20.04
12.12
20.16
20.16

If we displace the decimal point by one cypher to the left, we find again approximately whole numbers, which with one exception are almost as exact as the numbers given by P. Weiss. The numbers of magneton per molecule is rather high and it is not very surprising that in dividing for instance, 32,400 of $FeCl_3$ by 1,123.5 one finds approximately a whole number, 28.83 or 2.883 respectively. The large number of magnetons shown by the last two columns raises the question as to why those substances are so weakly magnetic, while nickel, being ferromagnetic, possesses at low temperatures only 3 magnetons. In addition, the numbers given by P. Weiss are based on the assumption that the magnetization of the pure salts and of the solutions varies according to Curie's law down to the absolute zero. As far as I know, this assumption has not yet been tested by experiments. Recently however Auguste Piccard[1] measured with great accuracy the susceptibility of oxygen at 20° C. and found for the moment of the atom: $7.8725 . 10^1$; dividing this number by 1123.4 one gets 7.007, a whole number again. But in this case H. Kamerlingh Onnes and A. Perrier have shown that at low temperatures the susceptibility of oxygen changes according to the law:

$$X_{\text{llg}} = \frac{2284}{\sqrt{T}} 10^{-6},$$

$$X_{\text{sol}} = \frac{1690}{\sqrt{T}} 10^{-6}.$$

If this element does not follow the law of Curie, solid salts and solutions will probably also show deviations, and at the same time the evidence in favor of the magneton will decrease. At all events the number of magnetons seems to vary in the atom of a given element like nickel, which contains 3 magnetons at low temperature, 8 at high temperatures, 9 at the limit of the alloys of iron and nickel, 16 in the solutions. In order to determine the magneton P. Weiss, abandoning the theory, has directly measured the molecular moments of iron, nickel and cobalt; Auguste Piccard, on the contrary, has used the theory in order to find the magneton in spite of the measurements of Kamerlingh Onnes and A. Perrier. If we assume that Curie's law holds down to the absolute zero, we find for the elementary moment of oxygen

$$m = 2.58 \cdot 10^{-20}.$$

The moment of each individual magneton of Weiss on the other hand would be equal to:

$$\frac{1123.5}{6.1 \cdot 10^{23}} = 1.85 \cdot 10^{-21}.$$

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[1] Archives de Genève, Tome XXXV., p. 480, 1913.

If we determine the molecular moments by means of Langevin's theory, we find values varying from $2.02 \cdot 10^{-22}$ to $5.15 \cdot 10^{-20}$ for substances so different among each other as oxygen, iron, magnetite and Heusler alloys. These values are of the order of magnitude which we should expect from the theory of quanta by Planck. Let us assume that the kinetic energy of a revolving electron $\frac{1}{2}mv^2$ is equal to a whole number z times hn, then we find:

$$\frac{m\omega^2 r^2}{2} = zhn = \frac{h\omega z}{2\pi},$$

$$\omega r^2 = \frac{hz}{\pi m}.$$

The moment of M of the revolving electron will be equal to:

$$M = iA = \pi r^2 \frac{e}{T} = \frac{e}{m}\frac{hz}{2\pi},$$

if we put $z = 1$, we find $M = 1.83 \cdot 10^{-20}$; for the frequency n we find $1.63 \cdot 10^{15}$, assuming $r = 1.5 \cdot 10^{-8}$. Why are these magnetons not sources of light? Not much importance must be attached to this approximate coincidence of $1.83 \cdot 10^{-20}$ with the moments determined by means of Langevin's theory. We find indeed about the same magnetic moment without the theory of the quanta, by calculating the velocity of the electron by the equation:

$$\frac{mv^2}{r} = \frac{e^2}{r^2};$$

putting $r = 1.5 \cdot 10^{-8}$; we get $n = 1.4 \cdot 10^{15}$; $M = 1.54 \cdot 10^{-20}$. And the question arises again, why does such a magneton not emit light? The difficulty might be removed by admitting a large number of electrons revolving in a circle, instead of one electron. The assumption of one single magneton, identically the same in all substances, seems to require much more experimental support, if it exists at all.

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Urbana, Illinois,
February 22, 1915.

ON THE PARTITION OF ENERGY BETWEEN MATTER AND ETHER.

By Louis Weisberg.

THE Rayleigh-Jeans formula for the distribution of energy in normal radiation (that of the black body) requires the total energy in the spectrum to be infinite.[1] Since bodies which require the addition of an infinite amount of energy to raise their temperature through a finite interval are quite foreign to our ordinary experience, it is clear that this formula must fail in that part of the spectrum where the energy per unit interval of frequency increases indefinitely with the frequency. The statement is often made that the validity of the formula throughout the spectrum is a necessary consequence of the "classical" dynamics.[2] If that be so, the classical dynamics is evidently unsuited to the treatment of radiation and kindred phenomena. It is useless to argue, as Jeans has done, that in our experiments we do not observe true equilibrium of radiation but radiation which has reached only a state of quasi-equilibrium, and that the final state (which requires perhaps an infinite time in which to establish itself) must conform to the formula.[3] For to accept such a view one's confidence in the theory must be greater than in the observed facts which it fails to explain. Jeans himself has abandoned this contention, and, if I do not misunderstand him, now asserts that we have come to a pass where some form of quantum is the only outlet. Poincare,[4] Jeans,[5] and, I believe, McLaren[6] (although I cannot follow his argument throughout) have arrived at results which are generally interpreted so as to involve the necessity of some form of discontinuity, if the total energy in the spectrum is to be finite. In the present paper I attempt to show that equipartition throughout the spectrum is not a necessary consequence of the classical dynamics, although a derivation of the sort of partition which would lead to Planck's formula I am unable to offer.

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[1] La Théorie du Rayonnement et les Quanta, Langevin and de Broglie, p. 15.

[2] Planck, Wärmestrahlung, 2d ed., p. 179. Poincaré, Dernières Pensées.

[3] Jeans, Phil. Mag., **10**, 91, 1905; **17**, 229, 1909.

[4] Poincaré, Journ. d. Phys. [5], **2**, p. 5, 1912.

[5] Jeans, Phil. Mag., **20**, 443, 1910.

[6] McLaren, Phil. Mag., **22**, 66, 1911; **23**, 513, 1912, **25**, 43, 1913.

It is an experimental fact that within a limited portion of the spectrum, the Rayleigh-Jeans formula is as good, if not better than, any other.[1] For high frequencies, it fails altogether. Let us call ν_0 that value of the frequency above which the formula cannot safely be applied. A dimensional argument is sufficient to show that the number of frequencies per unit volume in a radiation field between ν and $\nu + d\nu$ is equal to $k\nu^2 d\nu$, where k is a finite numerical factor. Consequently, if we assume absolute equipartition when ν is less than or equal to ν_0, the total amount of energy distributed in this manner is

$$\int_0^{\nu_0} kBT\nu^2 d\nu = \tfrac{1}{3}kBT\nu_0^3.$$

Thus there is equipartition only among part of the degrees of freedom, and they receive altogether at most a finite amount of energy. Lorentz has in fact proceeded after this phenomenological fashion in his derivation of the Rayleigh-Jeans formula.[2] To insure a finite value for ν_0 he supposes the existence of concealed coördinates whose function is simply to keep the energy finite. Although nothing is known about the nature of this concealed mechanism, the derivation of Lorentz is, in my opinion, the only one which can be regarded as at all satisfactory; for it will appear in a later paragraph that the statistical methods on which all the derivations rest become meaningless (and all the formulas illusory) if the total energy can become infinite.

Equipartition follows in general when the energy can be expressed in certain special forms as a function of the momenta and the coördinates of the system. According to McLaren, equipartition of kinetic energy is assured if for finite values of the energy all the momenta remain finite. Jeans states the proposition that if the energy (or any part of it) is expressible as a homogeneous function of the variables (or part of them), each of the corresponding degrees of freedom will possess on the average an amount of energy proportional to the absolute temperature. Doubtless there are any number of other conditions sufficient for equipartition. The really important thing to notice is that no one has proved the existence of equipartition among an infinite number of degrees of freedom, nor would such have meaning.

Let us consider an ensemble of dynamical systems, part of which may be material in nature and the rest ethereal. The systems comprising this ensemble differ in the configurations and velocities which they have at a given instant, not only infinitesimally, but it may be so as to embrace every conceivable combination of configurations and velocities. The first question concerns the distribution in phase of the whole number at any time, when it has been given for some one time. When the distribution is permanent in time, the ensemble is in statistical equilibrium. Suppose that the equations of motion are given by

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[1] Planck, Wärmestrahlung, p. 164.

[2] La Theorie du Rayonnement, l. c., Nuovo Cimento [5], **16**, 1908.

$$\frac{dx_r}{dt} = X_r, \quad (r = 1, 2, \ldots, n), \tag{1}$$

where X_r may be any function of $(x_1, x_2, \ldots, x_n, t)$. The nature of a system of equations of this sort is closely connected with the value of certain expressions to which Poincaré has given the name ***integral invariants***. The equations may be regarded as defining the motion of a point whose coördinates are $(x_1, x_2, \ldots, x_n)$ in a space of n dimensions. Any group of such points which at a time t_0 occupy a p-dimensional region V_0 will at a subsequent time t occupy another p-dimensional region V. A p-tuple integral taken over V is called an integral invariant if it has the same value at all times t; the number p is called the order of the integral invariant. Of particular importance are certain integral invariants whose order is equal to that of the system of equations. If the fractional number of systems out of the whole ensemble which at a given instant occupy the volume $\delta x_1 \ldots \delta x_n$ is $P\delta x_1 \ldots \delta x_n$, we must surely have at all times

$$\int \ldots \int P\delta x_1 \ldots \delta x_n = 1, \tag{2}$$

when the integrations are taken over all possible values of $(x_1, x_2, \ldots, x_n)$.[1] If $(\psi_1, \psi_2, \ldots, \psi_n)$ are a set of n arbitrary and independent constants of the integral equations of motion, the quantities $(x_1, x_2, \ldots, x_n)$ can be expressed in terms of these constants and the time. Then

$$\int \ldots \int P\delta x_1 \ldots \delta x_n = \int \ldots \int P \frac{\partial(x_1, x_2, \ldots, x_n)}{\partial(\psi_1, \psi_2, \ldots, \psi_n)} \delta\psi_1 \ldots \delta\psi_n = 1.$$

The condition that the integral (2) shall be invariant with respect to the time is

$$\frac{d}{dt}\left[P \frac{\partial(x_1, x_2, \ldots, x_n)}{\partial(\psi_1, \psi_2, \ldots, \psi_n)}\right] = 0,$$

or

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[1] The variation indicated by the symbol δ will always be one in which the time is fixed; thus it represents the passage from one contemporaneous path to another. If L is any function of $(x_1, x_2, \cdots, x_n, t)$, we have

$$\delta L = \sum_1 \frac{\partial L}{\partial x_r} \delta x_r,$$

while

$$dL = \sum_1^n \frac{\partial L}{\partial x_r} dx_r + \frac{\partial L}{\partial t} dt.$$

$$\frac{dP}{dt}\frac{\partial(x_1, x_2, \ldots, x_n)}{\partial(\psi_1, \psi_2, \ldots, \psi_n)} + P\sum_1^n \frac{\partial(x_1, x_2, \ldots, x_{r-1}, X_r, x_{r+1}, \ldots, x_n)}{\partial(\psi_1, \psi_2, \ldots, \psi_n)} = 0,$$

$$\frac{dP}{dt}\frac{\partial(x_1, x_2, \ldots, x_n)}{\partial(\psi_1, \psi_2, \ldots, \psi_n)} + P\sum_1^n \frac{\partial X_r}{\partial x_r}\frac{\partial(x_1, x_2, \ldots, x_n)}{\partial(\psi_1, \psi_2, \ldots, \psi_n)} = 0;$$

or finally

$$\frac{dP}{dt} + P\sum_1^n \frac{\partial X_r}{\partial x_r} = \frac{\partial P}{dt} + \sum_1^n \frac{\partial P}{\partial x_r}\cdot\frac{\partial x_r}{dt} + P\sum_1^n \frac{\partial X_r}{\partial x_r}$$

$$= \frac{\partial P}{\partial t} + \sum_1^n \frac{\partial(PX_r)}{\partial x_r} = 0. \qquad (3)$$

This equation shows that P must be a last multiplier for the system of equations (1). If the equations can be brought into the form

$$\frac{dq_r}{dt} = \frac{\partial H}{\partial p_r}, \quad \frac{dp_r}{dt} = -\frac{\partial H}{\partial q_r} + Q_r, \quad (r = 1, 2, \ldots, n),$$

where Q_r is a function only of $(q_1, q_2, \ldots, q_n, t)$, then $\Sigma_1^r\, \partial X_r/\partial x_r = 0$ and P is entirely independent of the time. In any event the condition

$$\frac{\partial P}{\partial t} = \sum_1^n \frac{\partial(PX_r)}{\partial x_r} = 0 \qquad (3a)$$

is sufficient for statistical equilibrium. It is not possible to make much progress without more definite information about the nature of the equations (1). A theorem due to Koenigs fortunately supplies just what is required for the problem in hand.

Corresponding to the system of equations (1) there exist an infinite number of integral invariants of order one.[1] Let

$$\int M_1\delta x_1 + M_2\delta x_2 + \ldots + M_n\delta x_n, \qquad (4)$$

where $M_1, M_2, \ldots, M_n$, are functions of $(x_1, x_2, \ldots, x_n, t)$, be one of these; the condition for this is

$$\frac{d}{dt}\left(\sum_1^n M_r\delta x_r\right) = \sum_1^n\left(\frac{dM_r}{dt}\delta x_r + M_r\frac{d\delta x_r}{dt}\right) = \sum_1^n\left(\frac{dM_r}{dt}\delta x_r + M_r\delta X_r\right) = 0,$$

since

$$\frac{d\delta x_r}{dt} = \delta\frac{dx_r}{dt} = \delta X_r.$$

Consequently,

$$\delta\left(\sum_1^n M_r X_r\right) = -\sum_1^n\left(\frac{dM_r}{dt}\delta x_r - X_r\delta M_r\right). \qquad (5)$$

The linear differential form in (4) may always be reduced, according as n is odd or even, to one of the two forms

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[1] Whittaker, Analytical Dynamics, Chap. 10.

$$p_1\delta q_1 + p_2\delta q_2 + \ldots + p_k\delta q_k - \delta W, \quad (2k + 1 = n), \tag{A}$$

$$p_1\delta q_1 + p_2\delta q_2 + \ldots + p_k\delta q_k, \quad (2k = n), \tag{B}$$

where $W, p_1, \ldots, p_k, q_1, \ldots, q_k$ are independent of one another. (A) and (B) are spoken of as the canonical forms. The proof of the possibility of this reduction may be found in any treatise on Pfaff's problem,[1] but the reduction in practice generally requires the solution of a finite number of differential equations, and so may involve serious difficulties. The existence of such reduced forms is, however, sufficient for the present argument.

Suppose then that the reduction has been performed on the differential form in (4) giving for example, the type (A), and that we take as new variables $W, p_1, \ldots, p_k, q_1, \ldots, q_k$, together with a number of other variables $u_1, u_2, \ldots, u_s$ such that s equals $n - 2k - 1$. The equations (1) become with these new variables

$$\frac{dW}{L} = \frac{dp_1}{P_1} = \ldots = \frac{dp_k}{P_k} = \frac{dq_1}{Q_1} = \ldots = \frac{dq_k}{Q_k} = \frac{du_1}{U_1} = \ldots = \frac{du_s}{U_s} = dt, \tag{6}$$

where $L, P_1, \ldots, P_k, Q_1, \ldots, Q_k, U_1, \ldots, U_s$ are functions of $W, p_1, \ldots, p_k, q_1, \ldots, q_k, u_1, \ldots, u_s$, and t. The condition (5) then transforms into

$$\delta\left(\sum_1^n p_rQ_r - L\right) = -\sum_1^n (P_r\delta q_r - Q_r\delta p_r).$$

On writing $H = \Sigma_1^n p_rQ_r - L$, this becomes

$$\delta H = \sum_1^n (Q_r\delta p_r - P_r\delta q_r),$$

which shows that

$$Q_r = \frac{\partial H}{\partial p_r} \quad \text{and} \quad P_r = -\frac{\partial H}{\partial q_r}.$$

The system (6), which is of course equivalent to (1), finally takes the form

$$\frac{dq_r}{dt} = \frac{\partial H}{\partial p_r}; \quad \frac{dp_r}{dt} = -\frac{\partial H}{\partial q_r} (r = 1, 2, \ldots, k) \tag{7}$$

$$L = \frac{dW}{dt} = \sum_1^n p_r \frac{\partial H}{\partial p_r} - H; \tag{8}$$

$$\frac{du_i}{dt} = U_i (i = 1, 2, \ldots, s). \tag{9}$$

If, however, the reduction of the differential form in (4) gives the type (B), one obtains after the same fashion

$$\delta\left(\sum_1^n p_rQ_r\right) = \sum_1^n (Q_r\delta p_r - P_r\delta q_r),$$

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[1] For example, Forsyth, Theory of Diff. Equations, Vol. 1.

and on placing $H = \Sigma_1^n p_r Q_r$,

$$Q_r = \frac{\partial H}{\partial p_r}, \quad P_r = -\frac{\partial H}{\partial q_r},$$

while

$$H = \sum_1^n p_r \frac{\partial H}{\partial p_r}.$$

In this case, H is a homogeneous function of the first order in the p's. Finally the equations now become

$$\frac{dq_r}{dt} = \frac{\partial H}{\partial p_r}; \quad \frac{dp_r}{dt} = -\frac{\partial H}{\partial q_r} (r = 1, 2, \ldots, k) \tag{7a}$$

with

$$\frac{du_i}{dt} = U_i (i = 1, 2, \ldots, s). \tag{9a}$$

The difference between the two cases (A) and (B) is seen to be simply that for the latter L in equation (8) becomes equal to zero. In either case the system (1) reduces to the Hamiltonian equations (7) or (7a) together with the subsidiary equations (9) or (9a). Nevertheless, I will henceforth assume that n is even. No serious limitation on the generality of the result can arise from this, for in ordinary dynamical systems the equations of motion are all of the second order, and these may evidently be reduced to a system of double the number of equations of the first order. Moreover, I shall assume that none of the quantities X_1, X_2, $\ldots$, X_n, M_1, M_2, $\ldots$, M_n contains the time explicitly; then $\Sigma_1^n (M_r X_r)$ is independent of the time and H is therefore an integral of the system (1).

Now construct a $2k$-dimensional space in which (p_1, p_2, $\ldots$, p_k, q_1, q_2, $\ldots$, q_k) are taken as coördinates. Then

$$\int \ldots \int P \delta p_1 \ldots \delta p_k \delta q_1 \ldots \delta q_k = 1, \tag{10}$$

if the integrations are taken over all possible values of these coördinates. Evidently the distribution given by P is permanent in time since by (3),

$$\sum_1^k \left(\frac{\partial \dot{p}_r}{\partial p_r} + \frac{\partial \dot{q}_r}{\partial q_r} \right) = 0.$$

For statistical equilibrium $\partial P / \partial t = 0$, and so

$$\frac{dP}{dt} = \frac{\partial P}{\partial t} + \sum_1^k \left(\frac{\partial P}{\partial q_r}\frac{dq_r}{dt} + \frac{\partial P}{\partial p_r}\frac{dp_r}{dt} \right) = \sum_1^k \left(\frac{\partial P}{\partial q_r}\frac{\partial H}{\partial p_r} - \frac{\partial P}{\partial p_r}\frac{\partial H}{\partial q_r} \right) = 0. \tag{11}$$

The last equation requires that P shall be some function of H. Among all the possible distributions satisfying (10) and (11) there is one which is unique in the possession of certain properties which are the foundation of some important relations to thermodynamics. This is closely akin to the distribution which Gibbs has called canonical.[1] If θ and ψ are constants, and θ positive, let

$$P = e^{\eta} = e^{(\psi - H)/\theta}. \qquad (12)$$

The main justification for employing this distribution lies in the theorem which will now be proved. Let us write $e^{((\psi-H)/\theta)+\Delta\eta}$ for any other distribution giving the same average value of H in the ensemble, where $\Delta\eta$ is an arbitrary function subject only to the limitation

$$\int\ldots\int e^{((\psi-H)/\theta)+\Delta\eta}\delta p_1 \ldots \delta q_k = \int\ldots\int e^{(\psi-H)/\theta}\delta p_1 \ldots \delta q_k = 1, \qquad (13)$$

and to that relating to the constant average value of H, namely

$$\int\ldots\int H e^{((\psi-H)/\theta)+\Delta\eta}\delta p_1 \ldots \delta q_k = \int\ldots\int H e^{(\psi-H)/\theta}\delta p_1 \ldots \delta q_k. \qquad (14)$$

It is to be proved that

$$\begin{aligned}\int\ldots\int\left(\frac{\psi}{\theta} - \frac{H}{\theta} + \Delta\eta\right) e^{((\psi-H)/\theta)+\Delta\eta}\delta p_1 \ldots \delta q_k \\ > \int\ldots\int\left(\frac{\psi}{\theta} - \frac{H}{\theta}\right) e^{(\psi-H)/\theta}\delta p_1 \ldots \delta q_k. \qquad (15)\end{aligned}$$

If (13) be multiplied by ψ/θ and (12) by $1/\theta$ and their difference subtracted from (15), the proposition to be proved reduces to

$$\int\ldots\int \Delta\eta e^{((\psi-H)/\theta)+\Delta\eta}\delta p_1 \ldots \delta q_k > 0,$$

which may be written in virtue of (14)

$$\int\ldots\int (\Delta\eta e^{\Delta\eta} + 1 - e^{\Delta\eta}) e^{(\psi-H)/\theta}\delta p_1 \ldots \delta q_k > 0.$$

Its truth follows at once from the observation that the parenthesis can never have a negative value and is zero only when $\Delta\eta$ is zero. Therefore, if an ensemble of systems is canonically distributed in phase, *i. e.*, according to (12), the average value of η or $\log P$ is less than in any other distribution having the same average value of H. If H can be identified with the energy, this becomes the distribution treated by Gibbs. As a matter of fact, it is easier to identify the average value of H with the energy rather than to identify H itself. In the cases we are considering,

$$H = \sum_1^k p_r \frac{\partial H}{\partial p_r},$$

so that for its average value in the ensemble, we have

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[1] Gibbs, Elementary Principles in Statistical Mechanics. The proposition which follows is in no essential different from that given by Gibbs (Chap. VII) except that H in the present case has not been identified with the energy. The proof is naturally similar to his.

$$\overline{H} = \frac{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\left(\sum_{1}^{k} p_r \frac{\partial H}{\partial p_r}\right)e^{(\psi-H)/\theta}\,\delta p_1 \ldots \delta q_k}{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} e^{(\psi-H)/\theta}\,\delta p_1 \ldots \delta q_k}.$$

On integration by parts,

$$\int_{-\infty}^{\infty} p_r \frac{\partial H}{\partial p_r} e^{(\psi-H)/\theta}\,\delta p_r = \theta \int_{-\infty}^{\infty} e^{(\psi-H)/\theta}\,\delta p_r$$

since the integrated terms vanish at the limits. (It is not necessary to take the limits infinite, for the probability of extremely large values of any p_r is so small that the integrated term is sure to vanish if only the limits are taken large enough.) Finally, the average value of H reduces simply to $k\theta$, each one of the terms $p_r(\partial H/\partial p_r)$ contributing an equal part, namely θ, to the sum. This is true, of course, only if the limits of integration for the p's are independent of the q's, and the limits of the various p's are independent of each other, as well as of the q's. Burbury would probably question the result on account of this assumption,[1] but I am not able to satisfy myself that his criticism hits the mark, and there is no general consensus that it does.

So far the influence of external bodies on the ensemble has not been considered, but for the sake of completeness in the identification of the average value of H it will be well to do so. Such bodies will not be regarded as forming part of the system, although their positions affect the forces acting on the system. Their influence may be sufficiently accounted for by the introduction of a proper number of coördinates, a_1, a_2, ..., etc. It is perhaps important to remark that, although these coördinates will affect the value of H and hence the distribution in the ensemble, none of our previous results will be affected. From (10) and (12),

$$e^{-\psi/\theta} = \int \ldots \int e^{-H/\theta}\,\delta p_1 \ldots \delta q_k.$$

In this equation, by which ψ is determined, the external coördinates, a_1, a_2, etc., contained implicitly in H, as well as θ, are regarded as constant in the integrations indicated. So by differentiation with respect to these quantities,

$$\begin{aligned} e^{-\psi/\theta}\left(-\frac{1}{\theta}d\psi + \frac{\psi}{\theta^2}d\theta\right) &= \frac{1}{\theta^2}d\theta \int \ldots \int H e^{-H/\theta}\,\delta p_1 \ldots \delta q_k \\ &\quad - \frac{1}{\theta}da_1 \int \ldots \int \frac{dH}{da_1} e^{-H/\theta}\,\delta p_1 \ldots \delta q_k \\ &\quad - \frac{1}{\theta}da_2 \int \ldots \int \frac{dH}{da_2} e^{-H/\theta}\,\delta p_1 \ldots \delta q_k -, \text{etc.}, \end{aligned}$$

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[1] Burbury, Kinetic Theory of Gases.

or multiplying by $\theta e^{\psi/\theta}$, and setting $A_1 = -dH/da_1$, $A_2 = -dH/da_2$, etc.,

$$\begin{aligned} -d\psi + \frac{\psi}{\theta}d\theta = \frac{1}{\theta}d\theta \int\dots\int He^{(\psi-H)/\theta}\delta p_1\dots\delta q_k \\ + da_1\int\dots\int A_1e^{(\psi-H)/\theta}\delta p_1\dots\delta q_k \\ + da_2\int\dots\int A_2e^{(\psi-H)/\theta}\delta p_1\dots\delta q_k + \text{etc.} \end{aligned}$$

Denoting by a horizontal line above the symbol the average value in the ensemble of that quantity, we may write this equation as

$$d\psi = \left(\frac{\psi}{\theta} - \frac{\overline{H}}{\theta}\right)d\theta - \overline{A}_1da_1 - \overline{A}_2da_2 \dots \tag{16}$$

From the definition of P,

$$\overline{\eta} = \frac{\psi - \overline{H}}{\theta}, \tag{17}$$

or

$$d\psi = d\overline{H} + \theta d\overline{\eta} + \overline{\eta}d\theta. \tag{18}$$

By comparison of (16), (17), and (18), we get

$$d\psi = \overline{\eta}d\theta - \overline{A}_1da_1 - \overline{A}_2da_2 \dots, \tag{19}$$

$$d\overline{H} = -\theta d\overline{\eta} - \overline{A}_1da_1 - \overline{A}_2da_2 \dots. \tag{20}$$

If we write $U = \overline{H}$, $F = \psi$, and $S = -\overline{\eta}$, these equations become identical in form with the usual thermodynamic equations connecting the energy U, the entropy S, the temperature θ, and Helmholtz's free energy F, the external work being given by

$$dW = \overline{A}_1da_1 + \overline{A}_2da_2 + \dots.$$

Although this matter of the thermodynamic analogies afforded by canonical ensembles is an extensive one, it must suffice to remark here that to human perception the average value of H will be indistinguishable from the total energy of the ensemble, θ from the temperature, and the average value of $-\eta$ from the entropy. The proposition stated in equation (15) is thus seen to be equivalent to the familiar one that in any change undergone by a system whose energy remains constant, the entropy cannot diminish.[1] The correspondence between these average results for the ensemble and the results of empirical thermodynamics increases rapidly as the number of degrees of freedom of the ensemble increases.

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[1] Many other propositions analogous to familiar theorems in thermodynamics are to be found in Gibbs' book (previously cited). The reader who wishes to satisfy himself further as to the close relation between U and $\overline{H}$ will find there processes carried out analogous to the passage of energy from bodies of higher to lower temperature, the complete Carnot cycle, etc.

Although we have developed these thermodynamic analogies only for part of the original ensemble (namely, those systems for which the differential equations could be brought into the Hamiltonian form), it is equally possible to derive such relations to thermodynamics for the whole of the original ensemble. But now the analogies do not involve exactly the same quantities. Nevertheless the correspondence becomes quite perfect on all points of importance as the number of degrees of freedom becomes very large. Consequently for an ensemble comprising both ether and matter, it becomes as close as we desire, provided our theorems do not fail in passing to the limit from an exceedingly great, but finite, number of degrees of freedom to the case where the number is infinite. While it is important to make this reservation and bear it in mind, it should be distinctly stated that all our experience constitutes evidence against such a possibility. Even if we do not regard natural phenomena as capable of being completely described by continuous equations, there is no reason to believe that an ultimate statistical explanation of the laws of thermodynamics cannot be found. At any rate, in none of the forms of quantum theory which have so far been advanced has this been questioned; and indeed, in most of them it is employed as a fundamental method of studying equilibrium conditions. We may therefore consider ourselves on ground relatively safe if we employ these considerations to draw our main conclusion.

We have found that in an ensemble made up of ether and matter together, part of the equations of motion can be reduced to the Hamiltonian form, and that if the corresponding degrees of freedom are taken together to form another ensemble, then the quantity whose average value is, to human senses, identical with the total energy of the reduced ensemble, is divided equally on the average among these degrees of freedom. It is not possible to prove such equipartition for the whole of the original ensemble, because the interaction of ether and matter cannot be adequately represented without the introduction of forces depending on the velocities. Any demonstration of equipartition, however, must require the forces to be derivable from a potential function, or otherwise to depend only on the coördinates and the time, but not on the velocities of the systems.[1] Of course, this does not mean that the forces cannot depend on the velocities at all; the Schering potential function affords an example in which the forces, while derivable from a potential (and satisfying the principle of energy), still depend on the velocities.[1] Accordingly, the energy of radiation, regarded as involving in its origin the interaction of matter and ether, can be distributed according to the Rayleigh-Jeans formula only through part of the spectrum, and only among a finite number of degrees of freedom. We need only examine our formulas to see that the canonical ensemble becomes illusory when the average value of H becomes infinite.[2] In order that the coefficient of probability P shall have any meaning, its value must lie between zero and unity. Then if θ is neither zero nor infinite (values which are of course never realized in any of our experiments) the value of P passes the bounds only if $\overline{H}$, and hence the total energy, becomes positively or negatively infinite. Hence only a finite amount of energy can be distributed according to the law of equipartition.

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[1] Jeans, Dynamical Theory of Gases, p. 176.

We are led thus to a complete reconciliation between experiment and dynamical theory so far as the equipartition of energy is concerned. That the interaction between matter and ether involves forces of character such as is sufficient to ensure that the whole system of equations (1) does not reduce to a purely Hamiltonian system without the subsidiary equations (9) or (9*a*), is, I believe, a logical inference from the fact that in none of our experiments do we find indications that energy tends to accumulate on the average in the ether at the expense of material energy.

The whole point of the matter may be made somewhat clearer by an illustration. Imagine the ether to be a fluid, such as is ordinarily studied in hydrodynamics, moving irrotationally through perforated matter imbedded in it. The motion of such a system has been investigated by Kelvin.[3] The kinetic energy of the whole system can be expressed as the sum of two parts, the first of which refers only to the matter embedded in the fluid, and the second only to the fluid. That part referring to the matter is a homogeneous quadratic function of velocities sufficient to specify its motion completely, while the other part is a homogeneous quadratic function of the cyclic constants of the fluid motion. From the kinetic energy the equations of motion can be formed after the Lagrangian method, and the coördinates which refer to the fluid turn out to be ignorable; so that by the formation of a modified Lagrangian function a system of equations is obtained which does not involve any of the coördinates of the fluid. Now if an ensemble of dynamical systems obeying these equations of motion is formed in the usual manner, it is found that the part of the kinetic energy depending on the velocities of the solids is divided equally among the respective degrees of freedom on the average. The remainder of the energy cannot be divided in any such manner, so far as I can see. Thus the solids and the fluid have each their proper energy, and in particular, that of the solids follows the equipartition law. The illustration is by no means perfectly suited, but it is the best I am able to offer. While it is hardly to be regarded even as a crude model of the complicated sort of mechanism necessary for the production of complete radiation, it serves to show that in the equilibrium between matter and ether all energy need not reside in the ether and that equipartition may exist among part—and only part—of the degrees of freedom.

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[1] Whittaker, Analytical Dynamics, p. 43.

[2] Gibbs, Statistical Mechanics, p. 110.

[3] Kelvin, Phil. Mag., 1873. A good account of this work may be found in Gray's Treatise on Magnetism and Electricity, Vol. I., p. 250 ff.

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THE MELTING-POINT OF TUNGSTEN.

By Irving Langmuir.

SEVERAL years ago (in 1910), during an extended investigation of the characteristics of tungsten filaments, the need arose for a simple means of determining the temperatures of the filaments. The setting up and calibration of special pyrometers would have seriously delayed the work in progress, and it was therefore decided to make as good an estimate of the temperatures as possible from data already available.

The candle power, power consumption, and resistance of the filaments were the quantities of most interest and most easily measured. Any one of these variables might serve as a basis for a temperature scale, but the candle power has marked advantages over the others. The resistance increases relatively slowly with the temperature and is very sensitive to the presence of impurities. The power consumption (wattage) increases more rapidly with temperature, but the law of variation was not definitely known. Furthermore, the wattage cannot be used to determine the temperature in case the filament is surrounded by a gas.

Rasch[1] had developed a relation between the total intrinsic brilliancy (H) of a black body and its temperature, which he expressed in the form

$$\log H = -\frac{A}{T} + B. \tag{1}$$

Haber[2] and Lucas[3] pointed out that this equation could be derived directly from the Wien equation by considering the total visible radiation to be replaced by an equivalent monochromatic radiation.

Crova,[4] however, had shown that with ordinary light sources having a continuous spectrum, it is possible to find a wave-length at which the monochromatic intensities of the different sources are proportional to the total intensities. Crova found this wave-length to be about .58 μ.

Nernst[5] tested Rasch's equation over the temperature range from

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[1] Ann. Phys., 14, 193 (1904).

[2] Thermodynamik technischer Gasreaktionen (1905), p. 271.

[3] Phys. Zeitsch., 6, 19 (1905).

[4] Comptes Rendus, 93, p. 512.

[5] Phys. Zeitsch., 7, 380 (1906).

1400° to 2300° and determined the values of the constants A and B. For this purpose Nernst filaments were measured, photometered, and set up in front of a black body furnace and brought to a temperature at which they disappeared against the background. The temperature of the furnace was determined by means of a carefully calibrated Wanner pyrometer, taking the melting-point of gold as 1337° K. (1064° C.) and C_2 of Wien's equation as 14,600. In this way he found that the temperature of a black body could be expressed as a function of its intrinsic brilliancy by the equation

$$T = \frac{11230}{5.367 - \log_{10} K}, \tag{2}$$

where K is the intrinsic brilliancy of the black body in Hefnerkerzen per sq. mm. The temperatures calculated from this equation agreed within 10° with those found by the Wanner pyrometer. The equation was also tested by comparing it with some data given by Lummer and Pringsheim[1] on the total brilliancy of a black body at three temperatures, 1449°, 1597°, and 1707°. In this case the calculated and observed temperatures agreed within 3°.

In order to apply the above equation to the determination of the temperature of filaments, the relative emissivity of the latter as compared to a black body must be known. The reflectivity of tungsten at room temperature (for $\lambda = .579\,\mu$) was found by von Wartenberg[2] to be 48.6 per cent. About the same time, Coblentz measured[3] the reflectivity of tungsten over a wide range of wave-lengths. For the wave-length $0.579\,\mu$ his result was 51 per cent., as against von Wartenberg's 48.6. From these results I have estimated that the reflectivity of tungsten would be about 49 per cent. for the Crova wave-length of $0.56\,\mu$.

At the time of the adoption of our temperature scale there were no data available for the reflectivity or emissivity of tungsten at high temperatures, but there was much evidence that in the case of other metals the optical properties were practically independent of the temperature even over wide ranges. This was especially well shown by the papers of Henning,[4] Rubens,[5] von Wartenberg[6] and Hyde.[7]

Even if the emissivity should vary slightly with the temperature, the errors that would be caused by assuming it to be constant would not be very serious. Thus from equation (2) it can be shown that a 1 per cent. error in the determination of the intrinsic brilliancy or in the assumed value of the emissivity would lead to errors in the temperature determination of only

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[1] See Rothmud, Z. anorg. Chem., 31, 140 (1902).

[2] Verh. deutschen phys. Ges. 12, 105 (1910).

[3] Phys. Rev., 30, 645 (1910); Bull. Bur. Standards, 7, 202 (1911).

[4] Zeitsch. f. Instrumentenkunde, 30, 1195 (1910).

[5] Verh. phys. Ges., 12, 172 (1910).

[6] Ber. physik. Ges., 12, 121 (1910).

[7] Astrophysical Journal, 36, 89 (1912).

0.4°	at	1000° K.
0.9°	at	1500
1.5°	at	2000
2.4°	at	2500
3.5°	at	3000
4.7°	at	3500

Therefore, even with a five per cent. change in the emissivity, the errors in the temperature scale would not exceed 24°.

We may then safely assume, as a first approximation, that the reflectivity of tungsten at all temperatures is 49 per cent. (for $\lambda = 0.56\,\mu$). The emissivity is thus 51 per cent.

If we let H be the intrinsic brilliancy of a tungsten filament in international candles per sq. cm., we have

$$K = \frac{H}{0.51 \times 0.9 \times 100} = .0218H.$$

Substituting this in (2), we obtain

$$T = \frac{11230}{7.029 - \log_{10} H}. \tag{3}$$

To determine H experimentally, it is only necessary to measure the candle power and divide this by the effective projected area of the filament. In practice the filament is usually in the form of a single loop, with the two legs nearly parallel. By photometering a filament of known diameter through a horizontal slit placed close to the lamp, and by making a simple geometrical correction, it is thus possible to determine the intrinsic brilliancy (H) with considerable accuracy. By the use of the slit errors due to the cooling effect of the leads are avoided.

The absorption of light by the bulb usually amounts to about 3 per cent. However, this is offset by the departure from Lambert's cosine law. Worthing[1] has shown that "the average brightness of a tungsten cylindrical filament, viewed normally to its axis from a distance, is about 3 per cent. greater than that of the central part." Since the reflectivity of tungsten as determined by von Wartenberg was for normal incidence, it is evident that the 3 per cent. increase in brilliancy from the above cause would just compensate for the bulb absorption. Therefore we may consider that H in equation (3) is the apparent intrinsic brilliancy of the filament, as actually photometered through the bulb.

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[1] Astrophys. Jour., 36, 354 (1912).

In determining the intrinsic brilliancy of tungsten filaments in lamps running at voltages considerably above their normal rating, values of H as high as 6,000 candles per sq. cm. were readily obtained. According to equation (3), this should correspond to a temperature of 3460° K. Since there was always perceptible blackening of the bulb under these conditions it is evident that the melting-point of tungsten must be considerably above 3460°. A note to this effect was published in 1911.[1]

Subsequent experiments in which the blackening of the bulb was prevented by inert gases showed that the intrinsic brilliancy at the melting-point is much higher than 6,000 candles per sq. cm.

The following tables gives some results obtained in the course of experiments on the dissociation of hydrogen.[2] The wire used was one of pure tungsten and had a diameter of .00706 cm. The candle power was measured while the voltage applied to the filament was gradually raised. The intrinsic brilliancy at the melting-point was calculated from the photometer setting at the time that the filament melted.

Table I.

Lamp No.	Gas in Lamp.		Candles Per Cm.².	Temp. ° K.
	Kind.	Pressure, mm.		
6220–1	H_2	760	7,020	3529
6220–3	H_2	200	6,450	3489
6179–1	N_2	720	7,030	3530
6179–3	N_2	200	7,120	3535
6179–4	N_2	50	7,060	3532
6179–5	—	0	6,750	3510
6321–2	H_2	720	7,050	3531
6321–1	H_2	200	7,350	3551
6435–5	H_2	750	7,460	3558
6394–4	H_2	200	6,850	3518
6220–6	—	0	6,790	3513
			Average.....	3528

In these measurements a Lummer-Brodhun photometer was usually used. To avoid the large differences in color between the two light sources, a blue glass screen was ordinarily placed on the side towards the standard lamp. This glass was calibrated by means of both a flicker and Lummer-Brodhun photometer.

The temperatures gives in the table were calculated according to equation (3).

The mean of these results is 3528° K. but since this method tends to give low results, weighted mean of 3540° K. would appear more probable. Previous experiments, made in 1911 with filaments in vacuum, had caused us at that time to adopt this figure (3540° K.) as the most probable value of the melting-point.[1]

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[1] Trans. Amer. Electrochem. Soc., 20, 237 (1911).

[2] Jour. Amer. Chem. Soc., 36, 1708 (1914).

OTHER DETERMINATIONS OF THE MELTING-POINT.

Determinations of the melting-point of tungsten by other investigators have usually led to lower results.

Waidner and Burgess,[2] by an extrapolation of the current-temperature curve of about 1400°, estimated the melting-point of tungsten to be 3470° K. (3200° C.). A little later[3] they redetermined the melting-point by similar methods and obtained 3350° K. (3080° C.).

Wartenberg[4] determined the black body melting-point of tungsten and by estimating the emissivity, concluded that the true melting-point must lie between 3070° and 3120° K. Subsequently,[5] he made use of his determination of the reflectivity[6] to recalculate the melting-point from the earlier data, and thus obtained 3170° K.

Pirani[7] found, from about 1400° to 2000° K., a linear relation between the logarithm of the temperature and the logarithm of current through a tungsten filament. Extrapolating by means of this relation and applying a correction of about 200°, he obtained for the melting-point 3500° K. ($C_2 = 14{,}500$). Two years later, von Pirani and Meyer[8] determined the black-body melting-point and from this calculated the true temperature by taking the emissivity (at $\lambda = 0.64\ \mu$) to be 51 per cent. Their result was 3270° K. ± 60° for $C_2 = 14{,}500$.

Shortly afterwards, v. Pirani[9] determined the emissivity of tungsten at high temperatures by means of a Holborn-Kurlbaum pyrometer and found (for $\lambda = 0.64\ \mu$) 48.5 ± 7.5 per cent., showing that for tungsten the emissivity at high temperatures cannot be greatly different from that at room temperature (51 per cent.).

Forsythe[10] used two different methods in determining the melting-point.

In the first, an optical pyrometer was sighted on the inside of a carbon tube vacuum furnace containing a hairpin filament of tungsten. Thirteen observations of the melting-point gave for an average 3247° K. ($C_2 = 14{,}500$).

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[1] This result was published in 1913, Jour. Amer. Soc., 35, 944 (1913).

[2] Bull. Bur. Standards, 2, 319 (1906).

[3] J. physique, 6, 380 (1908).

[4] Ber. deutsch. chem. Ges., 40, 3287 (1907).

[5] Verh. d. physik. Ges., 12, 121 (1910).

[6] L. c.

[7] Verh. d. physik. Ges., 12, 310 (1910).

[8] Verh. d. physik. Ges., 14, 426 (1912).

[9] Physik. Zeitsch., 13, 753 (1912).

[10] Thesis, Univ. Wisconsin, 1911.

In the second method, the black-body melting-point was determined by "balancing the lamp filaments photometrically against the heater tube of the furnace and taking the temperature with the optical pyrometer." In other cases, a tungsten strip was mounted in an exhausted water-cooled brass vessel with windows. Twelve determinations gave an average of 3070° K. for the black-body melting-point. This was then corrected for the difference between black body and true temperatures as found by extrapolation from observations on wedges run up to nearly 3000°. The true melting-point determined in this way was 3300° K., which was considered to be too high.

Ruff[1] has published several results on the melting-point of tungsten

2923° K. Ruff (Ber. d. chem. Ges., 43, 1564 (1910)).
2858° K. Ruff and Goecke (Z. angew. Chem., 24, 1461 (1911)).
2923° K. Ruff (Z. angew. Chem., 24, 2245 (1911)).
3213° K. Ruff (Z. angew. Chem., 25, 1894 (1912)).

as determined in carbon tube vacuum furnaces.

From the results obtained by all these investigators, the most probable value of the melting-point would appear to lie between 3200 and 3300° K.

This, however, is about 300° lower than the value we have found by the measurement of the total intrinsic brilliancy.

SOURCES OF ERROR.

To determine, if possible, the cause of this discrepancy, Dr. E. Q. Adams, of this laboratory, nearly three years ago made careful calculations of the temperature errors that might be due to the use of total brilliancy rather than monochromatic intensity. This calculation was based on Nutting's recalculation of König's data on visibility,[2] Wien's equation, and Coblentz's data on the reflectivity of tungsten.

The equation (2) given by Nernst (and therefore also equation 3) corresponds to a "Crova wave-length" of 0.565 μ (taking $C_2 = 14{,}600$) Dr. Adams calculated that the true Crova wave-length should vary with the temperature of the light source, being about 0.575 μ at 2400° and 0.555 at 3500° K. The errors in the temperature scale due to taking a constant wave-length (0.565 μ) are found never to exceed 20.

A similar conclusion may be drawn from Ives's analysis of Crova's method of photometry.[3] According to Ives, the error in intensity due to taking a constant Crova wave-length of 0.565 μ should not exceed about 3 per cent. in the range from 2000° to 6000° K. We have seen that 3 per cent. error in candle power would lead to an error in temperature of only 14° at 3500°.

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[1] These results are:

[2] Bull. Bur. Standards, 5, 261 (1909) and 7, 238 (1911).

[3] Phys. Rev., 32, 316 (1911).

It is therefore evident that the discrepancy of 300° cannot be due to the use of Crova's method. The other possible sources of error are: (1) a wrong value for the emissivity; (2) a wrong value for the constant in the denominator of Nernst's equation (2).

Even if the emissivity should be 70 per cent. instead of 51 per cent. the melting-point by the total photometric method would still be 3400°. The whole of the discrepancy therefore cannot be explained in this way.

On the other hand, to account for the discrepancy by an error in the constant of Nernst's equation, it would be necessary to assume that the candle powers determined by Nernst were 50 per cent. too low, or that this temperature scale was in error by 44° at the melting-point of gold and 100° at the melting-point of platinum.

The above considerations all tend to confirm the substantial accuracy of the value of 3540° K. as the melting-point.

There does not seem to be any single cause that could account for all the lower values obtained by others. Into many of the methods, however, one factor has entered which tends, according to our experience, to lower the melting-point. This is the presence of vapors of carbon or compounds containing carbon.

In the manufacture of squirted tungsten filaments the latter were sintered by heating to a high temperature in hydrogen. It has often been noticed that the presence of even minute amounts of hydrocarbon vapors in the hydrogen very materially lowers the melting-point and increases the specific resistance. When a filament is quickly raised to its melting-point under these conditions, it is sometimes found that the surface layer melts and runs together in uniformly spaced beads along the wire, showing that the surface layer has a much lower melting-point than the pure tungsten core. These effects are noticed equally well with drawn tungsten wire as with squirted filaments.

Other experiments have shown conclusively that carbon not only lowers the melting-point and raises the resistance, but increases the emissivity. The quantities of hydrocarbon vapor given off by vaseline or stop-cock grease at room temperature in vacuum are sufficient to bring about these changes in a very short time.

The presence of carbon vapors in the experiments of Ruff and in those of Forsythe (1st method) could readily account for a lowering of the melting point of 300° or more. This objection does not apply, however, to Forsythe's determination of the black-body melting-point of the filament of an evacuated lamp. Only the results of one experiment of this kind are recorded. The presence of carbon vapors, however, may have led to too high a value for the emissivity. Calculating from the difference between the black body and the true temperatures given by Forsythe, the emissivity at the melting-point was found to be 61 per cent. If the value 51 per cent. had been taken instead of 61 per cent., the result would have been 3395°, instead of 3303°.[1]

At a later date, Mendenhall and Forsythe[2] gave the results of determinations of the emissivity of tungsten at high temperatures. They concluded that the emissivity varies from 45 per cent. at 1400° K. to 66 per cent. at 3200° K. In these experiments, however, hydrocarbon vapors were present and there is a possibility that the errors were caused by the opening of a crack at the back of the V made from the two strips of tungsten.

New Experiments on Melting Point of Tungsten.

In view of the difficulty of reconciling the value 3540° with the other determinations, it was decided to redetermine the melting-point by methods which would be free from the objections of the total photometric method. An essential part of such work is the determination of the emissivity at high temperatures.

Two methods were used. In the first, the black body melting-point of large filaments in nitrogen was determined and the emissivity was found from measurements on helically wound filaments of various sizes in vacuum and in nitrogen. The second method consisted of measuring the brilliancy of a surface of molten tungsten and simultaneously determining the brilliancy of the image of a second surface of molten tungsten reflected in the first. Thus the reflectivity of molten tungsten was determined directly.

Pyrometer.

The pyrometer used was of the Holborn-Kurlbaum type and resembled very closely that used by Worthing and Forsythe in the Nela Research Laboratory.[3]

To avoid the errors due to diffraction, pointed out by Worthing and Forsythe, no changes were made in the settings of the apparatus throughout the whole series of measurements. Focusing was always done by moving the background lamp.

Screens.

Several nearly monochromatic screens were used in the eyepiece of the telescope.

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[1] If the emissivity be taken as 0.46 per cent., the value found as a result of the present investigation, Forsythe's data would lead to a melting-point of 3450°.

[2] Astrophys. Jour., 37, 380 (1913).

[3] Phys. Rev., 4, 163 (1914).

Screen a.—This consisted of a double thickness of Schott and Gnossen's red glass No. 4512. This screen was kindly given me by Dr. Forsythe and is the same as that used in most of his work. Examined with a spectroscope, using a strong source of light (high efficiency tungsten lamp), the transmitted band is seen to extend from .637 to .730 μ, with a maximum at .658 μ. The center of gravity is seen to lie above the maximum, and by observation was estimated to lie at .661 μ.

Screen b.—Wratten and Wainwright green gelatin screen No. 74 (also marked *e''*). This transmits from .514 to .573 with a maximum at .539.

Screen c.—A combination of Wratten and Wainwright screens 15 and 45. This transmits a narrow symmetrical band with the limits 0.513 and .553. The maximum transmission and the center of gravity appear to be at 0.530.

To determine by independent means the equivalent monochromatic wave-lengths of these screens, the relative brilliancy of a large nitrogen filled lamp (filament straight, not helically wound) was measured by a Lummer-Brodhun photometer at a series of different temperatures, using successively the different screens in the eyepiece.

According to Wien's law, the intensity E_1 of the light of wave-length λ_1, emitted by a body at any temperature T, is given by

$$\log E_1 = a_1 - \frac{b}{\lambda_1 T},$$

where $b = .4343C_2$ and a_1 is a constant. For any other wave-length λ_2, the intensity E_2, will be given by

$$\log E_2 = a_2 - \frac{b}{\lambda_2 T},$$

where a_2 may be different from a_1.

Eliminating T from these equations, we obtain:

$$\log E_1 = \left(a_1 - a_2\frac{\lambda_2}{\lambda_1}\right) + \frac{\lambda_2}{\lambda_1}\log E_2.$$

Therefore, by plotting $\log E_1$ against $\log E_2$ a straight line of slope λ_2/λ_1 should be obtained.

The values of E obtained by photometering the large lamp with the various screens were plotted in this way. By assuming that the equivalent wave-length λ of screen c was 0.530, the wave-lengths of the others were found from the slopes of the lines on the plot.

The values for the equivalent wave-lengths found in this way are given in the second column of the following table, together with those estimated by direct spectroscopic examination (third column):

Screen.	By Photometer.	By Spectroscope.
a	0.667 μ	0.661 μ
b	0.537	0.539
c	[.530]	.530

Only the screens *a* and *b* were used with the pyrometer. The wavelengths used in the calculation of the temperatures were those found by the photometric method.

Calibration of Pyrometer.

The first step in the calibration of the pyrometer was the determination of the relation between the luminous intensity of the pyrometer filament and the current flowing through it. This was accomplished by means of three rotating sectors (ratios 1/5, 1/20 and 1/100) and also by comparison with the large nitrogen filled lamp which had previously been photometered through the screens, *a*, *b*, and *c*. Since the lamp had been photometered through a slit which screened off the cooled portions of the filament near the leads, the intensities determined by the photometer should be proportional to those observed in the pyrometer.

The range over which the lamp had been photometered was a wide one, corresponding to temperatures from 1850° to 3040° K. The intensity between these limits increased about ninety-fold with the red screen and nearly 300-fold with the green. By the use of the sectors, it was therefore possible to obtain four curves of the relation between intensity and pryometer current, which overlapped one another to such an extent that the accuracy was much higher than could have been obtained without the sectors. Curves of this character were prepared with both screens *a* and *b*.

The second step was now to determine the current through the pyrometer lamp corresponding to one or more fixed temperatures.

A porcelain tube black-body furnace was set up to calibrate against the melting-point of gold.

Another furnace, consisting of a molybdenum wound alundum tube in a hydrogen atmosphere, was used for the melting-point of copper.

Several determinations of the black-body melting-point of platinum were made.

Finally, the pyrometer was checked against a heavy-filament, evacuated tungsten lamp which had been calibrated by Dr. W. E. Forsythe against a black-body furnace at the melting-point of gold and at the melting-point of palladium.

In comparing the observations at these different temperatures, application was made of Wien's law using $C_2 = 14,390\,\mu$. This value was chosen as a weighted mean of Warburg's value 14,370[1] and Coblentz's value 14,456.[2]

The temperature scale was then so fixed that the mean of the results obtained for the gold melting-point agreed with Day and Sosman's value, 1062.4° C. In the following table the "observed melting-points" were those found with the pyrometer calibrated in this way. In each case, screen *a* was used.

TABLE II.

Calibration of Pyrometer.

	Observed Melting Point. °K.	Actual Melting Point.	
		°K.	°C.
Gold	1335	1335.4	1062.4[3]
"	1332	"	"
"	1338	"	"
Copper	1358	1356	1083[3]
Platinum (in nitrogen)	2022	2026	1753[3]
" (in nitrogen)	2024	2026	1753
" (in air)	2040	2026	1753
" (in air)	2037	2026	1753
Gold (Fosythe's lamp)	1338	1335.4	1062.4[4]
Palladium (Forsythe's lamp)	1824	1822.2	1549.2[5]

The data for platinum were found by determination of the black-body melting-point of short loops of pure platinum wire (.025 cm. diameter). Three of these were mounted in incandescent lamp bulbs which were exhausted and filled with pure nitrogen. One of these bulbs was accidentally cracked so that air entered the bulb. With each of these lamps, after the platinum wire had been melted, the bulb was broken open and its absorption was determined (usually about 9 per cent.).[6] The fourth determination of the platinum melting-point was made with a loop of wire in the open air. In each case, by careful exploration of the temperatures along the wire while somewhat below the melting-point, it was possible to observe the wire at the place where it ultimately melted.

From these black-body melting-points the "true" melting-points were calculated by taking the emissivity (for $\lambda = .667$) to be 33 per cent., the value recently given by Burgess and Walterberg.[7]

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[1] Ann. Phys., 40, 609 (1913).

[2] Jahrb. d. Radioakt., 10, 340 (1913).

[3] Day and Sosman, PHYS. REV., 30, 412 (1910).

[4] Day and Sosman, PHYS. REV., 30, 412 (1910).

[5] Day and Sosman, Journ. de Physique, 5, 899 (1912).

[6] This 9 per cent. includes reflection from the inner and outer surfaces of the bulb and is not all due to absorption. With the photometer the correction for bulb absorption is much less (3 per cent.), because the reflected light is not lost.

[7] PHYS. REV., 4, 546 (1914).

It is interesting to note that the melting-points determined in air are about 15° higher than those found in nitrogen. If, however, the emissivity in air had been 35.6 per cent. instead of 33 per cent., this difference would be accounted for. Through the pyrometer the surface of the platinum wire appeared to be rather rough, or pitted, as compared with the usual surface of tungsten wires. Considering the uncertainty in the emissivity, the agreement with the results of Day and Sosman is very satisfactory.

Having thus calibrated the pyrometer with screen *a* it was now calibrated with screen *b* by setting up the black-body furnace before the pyrometer and comparing the readings obtained with the two screens.

Emissivity of Solid Tungsten.

Upon throwing an enlarged image of the helically wound filament of a nitrogen filled lamp upon a screen, one is struck by the relatively large difference in the intensity of the light from the interior and exterior parts of the helix. With a portable Weber photometer the intrinsic brilliancy of these adjacent parts of the image were found to differ by a ratio as large as 1 : 2. Examination of the image seemed to show that this effect was not due to a difference of temperature between the inside and outside, for there were small areas on the inside which were approximately the same intensity as the outside surface and on the other hand, there were strips along the edges of the outside portions which were nearly as bright as the brightest portions inside.

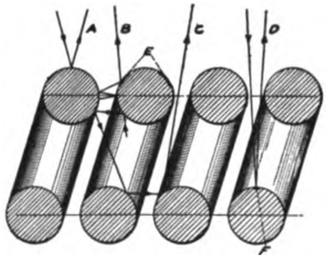

Fig. 1.

The difference in intensity appeared to be due entirely to reflection of light from one portion of the helix to another. In Fig. 1 is represented a longitudinal cross-section of a filament of this kind. The typical paths followed by light rays reflected from such a filament are shown by the letters *A*, *B*, *C*, *D*. In the case *A* there is no opportunity for multiple reflections and brilliancy of the surface is therefore the same as that of a straight filament. The ray *B*, however, is reflected several times and the intensity therefore approaches closely to that of a black-body at the same temperature. It is evident that narrow strips on each side of the wire, as indicated by the heavy lines at *E*, should appear to be of higher intensity. Similarly, the ray *C* is reflected many times, while *D* is only reflected once. Therefore there should be a very narrow strip in the position indicated by *F*, where the intensity is as low as that at *A* and on each side of this the intensity should be high.

Examination of an enlarged image of the filament clearly shows the presence of the dark and light portions in the positions to be expected.

Furthermore, if the helically wound filament is in the shape of a V with the two legs close together, the reflection of one leg in the other is clearly visible and the intensity of the reflected image can be measured approximately.

That the variations in the intensity cannot be due to temperature differences can be calculated readily from the known energy input and from Worthing's data[1] on the heat conductivity of tungsten at high temperatures. Even if we assume the whole of the heat to be generated at the inner side of the wire and all radiated from the outer surface, the difference in temperature for a wire 0.5 mm. in diameter would not exceed about 5° with the filament at 2900°. Actually, however, the effect must be much less than this, especially with the smaller wires and lower temperatures.

A determination of the relative brilliancy of the brightest and darkest portions of a helically wound filament may therefore serve as a basis for calculating an approximate value for the emissivity. However, because of the departure from true black body conditions within the helix, this value will always be somewhat higher than the actual emissivity.

Three lamps were made up with helically wound filaments from wires of different sizes. The filaments were wound so as to be all geometrically similar. Thus, in each case, the mandrel on which the helix was wound had a diameter 1.5 times that of the wire used, and the pitch of the helix was 1.33 times the diameter of the wire, so that the space between consecutive turns was 0.33 of the diameter. The diameters of the three wires were 0.202, 0.305 and 0.635 mm.

Each filament consisted of a V containing 30 turns per leg. The filaments were mounted in large bulbs filled with pure nitrogen. The results obtained with these lamps are given in Table III. The currents given are those which were necessary to heat the helical filament to the temperature indicated. The last column gives the ratio between the brilliancy of the outside part of the helix and that of the brightest portion inside. If strictly black-body conditions prevailed inside the helix, this ratio would be the true emissivity of tungsten. Actually, however, the emissivity must be less than this.

The fact that the emissivity found in this way does not vary appreciably with the diameter of the wire nor with the temperature, is confirmation of our theoretical conclusion that the difference in brilliancy between the inner and outer portions cannot be due to a difference in temperature.

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[1] PHYS. REV., 4, 535 (1914).

TABLE III.

Emissivity of Tungsten by Observation of Helical Filaments.

Lamp No.	Diam. of Filament, Cm.	Current, Amps.	Temp. of Filament.	Apparent Screen, *a*.	Emissivity Screen, *b*.
1	0.202	3.04	2040° K.	.50	—
		4.52	2720	.47	—
2	0.305	7.66	2050	.52	—
		12.64	2870	.51	—
3	0.635	16.26	2030	.51	—
		27.1	2820	.52	—
4	0.635	7.7	1430	.507	.512
		15.3	2070	.497	.538
5	0.635	9.6	1450	.465	.481
		16.0	2060	.468	.485
		28.4	2950	.465	.502
6	0.51	15.0	2320	.510	—
		20.0	2900	.486	—
		22.0	3110	.481	—

The helical filaments of lamps 1, 2, and 3 were wound with such a large spacing that the conditions inside the helix did not approach very closely to those in a black-body. To overcome this difficulty as far as possible, lamps 4, 5, and 6 were made up with helical filaments in which the spacing between turns was made as small as was found practicable without too great danger of short-circuiting adjacent turns. The average spacing was roughly $\frac{1}{4}$ of the diameter of the wires. Lamp 4 was evacuated and the tests were made with the lamp in this condition. Lamps 5 and 6 were filled with pure nitrogen. The filaments in each case were aged before the measurements were made, as preliminary tests showed that unless this was done the emissivity was much higher (about 0.60).

The emissivities obtained with lamps 4, 5 and 6 were consistently lower than those found with the first three lamps. Judging from the data obtained with lamp No. 5, the true emissivity must be 0.465, or lower for a wave-length $\lambda = 0.667$ (screen *a*) and 0.485 or lower for $\lambda = 0.537$.

By another method, which will be described below, the emissivity of molten tungsten was measured and found to be .425, while the emissivity of solid tungsten was seen to be distinctly greater than that of the liquid.

From these considerations, we may adopt 0.46 as the most probable value of the emissivity of solid tungsten for $\lambda = .667$. For green light ($\lambda = .535$), we may take the emissivity to be 0.48. These values are in good agreement with Littleton's[1] determination of the reflectivity of ductile tungsten at room temperature. Littleton found $R = 0.545$ for $\lambda = .589$, which corresponds to an emissivity of .455 for this wave-length. Evidently, the reflectivity of tungsten does not change appreciably over the whole range from room temperature up to the melting-point.

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[1] Phys. Rev., 35, 308 (1912).

Melting Points of Tungsten Filaments.

Several lamps were made up containing short filaments (about 6 cm. long) mounted in the form of a single hair pin loop. The bulbs were exhausted while heated an hour to 360° C., filled with pure, dry nitrogen and sealed off.

These lamps were set up, one by one, on the pyrometer, the temperature of the filament was gradually raised to about 3100°.

The temperatures of the filament were not quite uniform, the hottest parts usually being about two thirds of the way from the tip to the lead. The lower portion was cooled somewhat more by convection currents than the upper part, while the upper third was cooled by conduction of heat to the leads. By tilting the lamp slightly, so that one leg of the filament was vertical while the other was somewhat inclined, the temperature of the vertical leg became distinctly higher than that of the other. The hottest point of each filament was located by exploration with the pyrometer and it was thus always possible to sight the pyrometer on the portion at which melting first occurred. The life of the filaments at the highest temperature was so greatly increased by the surrounding atmosphere of pure nitrogen that the temperature could be raised very slowly to the melting-point. Usually, the actual melting lasted for several seconds, so that accurate pyrometer settings could be made.

TABLE IV.

Lamp No.	Filament Diameter, Cm.	Screen *a*.	
		Temp. of Melting Point.	
		Black Body, $\lambda = 0.667$.	True.
7	.0254	3134° K.	3532° K.
8	.0254	3129	3526
9	.0254	3137	3535
10	.0127	3111	3503
11	.0127	3143	3544
12	.0127	3149	3552
Average		3134	3532

After the filament had burned out the bulbs were broken open and the absorption coefficient of the bulb was determined. In every case this was approximately 10 per cent.

Table IV. gives the results obtained in this way. The black-body temperatures have been corrected for bulb absorption. The true temperatures were calculated from black-body temperatures by taking the emissivity (for $\lambda = .667\ \mu$) to be 0.46.

The filaments of lamps 9, 10, and 12 were of exceptionally pure tungsten, while the filaments of lamps 7, 8, and 11 were of "thoriated tungsten"; that is, tungsten made from a mixture of pure tungsten with about 1½ per cent. of thorium oxide. It is evident that the presence of the thorium oxide does not appreciably lower the melting-point.

Determination of Emissivity and Melting-Point by Means of an Arc between Tungsten Electrodes.

An alternating current arc was made to pass between two tungsten electrodes in nitrogen at atmospheric pressure. With sufficiently high current density the ends of both electrodes melted and formed mirror-like convex surfaces in which multiple reflections of the two electrodes could be seen. These surfaces were maintained above the melting-point without perceptible change, for periods of half an hour and more, during which time the intrinsic brilliancy of the molten tungsten and of the successive reflected images were repeatedly measured. This gave a direct determination of the reflectivity of molten tungsten and a simultaneous measurement of the black-body temperature.

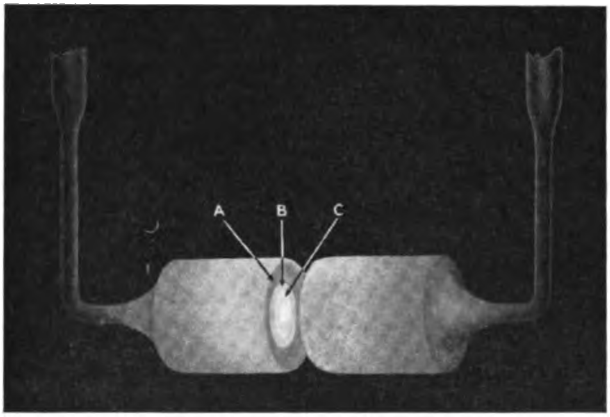

Fig. 2.

The shape and relative positions of the two electrodes are sketched in Fig. 2. The dimensions of the electrodes were approximately as follows: greatest diameter 2.0 mm.; distance apart 1 mm.; least diameter 0.3 mm.; length of large part 2.5 mm.

The extent to which the ends melted could be controlled by adjusting the current. At first only a small wandering spot of molten metal was seen, but with larger currents the end of each electrode became uniformly melted and assumed a slightly convex form in which the opposite electrode formed a beautifully reflected image (*B*, Fig. 1) of elliptical shape. Inside of this image could be seen a series of concentric ellipses which constituted the successive multiple reflections between the two electrodes. Altogether, four such images could be distinguished, although only the first two were large enough to allow accurate determinations of their intrinsic brilliancy.

The molten tungsten was readily distinguishable in the pyrometer from the solid. In the first place, the solid tungsten always appeared brighter than the molten tungsten in contact with it. Furthermore, the crystalline structure of the solid could be clearly seen, especially if it had previously been melted.

The surface of the molten tungsten was always perfectly uniform and entirely devoid of visible structure.

The arc itself was practically non-luminous. A reading of the pyrometer when set on the space between the two electrodes showed an intrinsic brilliancy only 1.0 per cent. of that of the electrodes. This measurement gives the scattered light in the pyrometer as well as from the arc itself.

If we let r be the reflectivity of tungsten and take as the unit of intrinsic brilliancy that of the surface of molten tungsten at *A* (Fig. 2), then the brilliancy of the first image (*B*) should be $1 + r$ and that of the second image (*C*) should be $1 + r + r^2$. The average of about twenty closely agreeing determinations of intrinsic brilliancy on two pairs of electrodes using the screen *a*, gave the result shown in Table V.

TABLE V.

Reflectivity of Molten Tungsten

Screen *a*.

Surface.	Relative Brilliancy.		Calculated $r = .575$.
	Observed.	Theoretical.	
A	1.00	1.00	1.00
B	1.59	$1 + r$	1.575
C	1.89	$1 + r + r^2$	1.905

The observed ratios are in good agreement with the theoretical relation if we take the reflectivity r to be 0.575. This corresponds to an emissivity of .425 for molten tungsten ($\lambda = 0.667$).

In measuring the black-body temperature of the molten tungsten in determining the melting-point, care was taken to observe a portion of the surface close to the edge of the molten pool, to avoid errors due to superheating of the liquid. The observations were made with the line of sight as nearly normal to the surface of tungsten as possible, for the departure from Lambert's cosine law would otherwise cause errors.

Several determinations of the *black-body melting-point* with the red screen (*a*) gave, after correction for bulb absorption (10 – 17 per cent.), an average of 3124° K. for $\lambda = (.667)$.

This corresponds to a true temperature of 3566° K. if we take the emissivity of molten tungsten (for $\lambda = .667$) to be 0.425.

Only one determination of the black-body temperature was made with the green screen (*b*) and this gave 3322° K. (for $\lambda = 0.535$).

The emissivity of molten tungsten was not measured with the green screen, but if we assume that the *difference* between the emissivity for green and red is the same for molten as for solid tungsten, we may take 0.445 as the emissivity of the liquid for green light. This gives for the true temperature of the melting-point 3550° K. a value 16° lower than that found with the red screen.

Discussion of Results.

Let us now examine the sources of error involved in the three methods we have used.

The errors of the total photometric method we have already discussed, and our conclusion that this method should not be seriously in error is amply verified by the results obtained by the last two methods. Thus, by the total photometric method we have obtained 3540° as the most probable value for the melting-point, while the *pyrometer* observations on filaments have given an average of 3532° and the observations on the arc electrodes, 3566°.

The main sources of error in the pyrometer methods are:

1. Errors in calibrating at the gold or palladium melting-point.
2. Errors in determining the equivalent monochromatic wave-length of the screens.
3. Errors in the constant C_2 of Wien's equation.
4. Errors in calibrating the foreground filament.
5. Errors in determining the emissivity.
6. Errors in taking the pyrometer readings.

The errors in calibrating against the gold and palladium melting-points are probably not over 2 or 3° at the gold point 1335° or 5° at the palladium point. An error of 1° at the gold point would cause an error of 7° at the tungsten melting-point.

Probably the greatest source of error is in determining the equivalent wave-length for the screens.[1] If we assume that the calibration at the palladium point is correct, then an error of 1 per cent. in determining this wave-length (or a 1 per cent. error in C_2) would cause an error of 32° at the tungsten melting-point. The value $\lambda = 0.667$, which we have taken for the red screen, is perhaps a little too high, although it is certain that it cannot be less than 0.661. There is thus a possibility that this wave-length is nearly 1 per cent. too high. If so, the values for the melting-point should be lowered about 30°.

An error of 1 per cent. in measuring the brilliancy of a filament involves an error of 6° with the red screen, or 5° with the green at the tungsten melting-point.

The melting-points determined by sighting on filaments should tend to be low, whereas those found by observing molten tungsten should be high. The most probable value is the mean of the two. Taking the pyrometer measurements on the filaments and the arc electrodes (with red screen only), we thus obtain 3549°. In view of the fact that the equivalent wave-length of the screen may have been taken too high, we can hardly do better than accept as a final result, the value we have previously obtained by the total photometric method, namely, 3540°.

Taking all the known sources of error into consideration, it would seem hardly possible that the error involved in these results should exceed ± 30°.

SUMMARY.

Observations on evacuated and on gas-filled tungsten lamps indicate that the intrinsic brilliancy of solid tungsten, at a temperature just below the melting-point, is about 7,200 international candles per sq. cm.

According to Rasch's equation, with constants determined by Nernst, and with an emissivity determined by v. Wartenberg, Coblentz and v. Pirani, this intrinsic brilliancy should correspond to a temperature of 3540° K. for the melting-point.

An analysis of the sources of error of this method gives no reason to suspect an error greater than 50°.

Two other methods for determining the melting-point by means of a Holborn-Kurlbaum pyrometer are also used.

In the first method, the black-body temperature of tungsten filaments heated to their melting-point is determined, while the emissivity is measured by observations on helically wound filaments.

In the second method, an alternating current arc is passed between two tungsten electrodes placed close together in an atmosphere of nitrogen, and the current is increased until the surfaces of both electrodes are molten. By measuring the intrinsic brilliancy of the molten surface, as well as that of the image of one electrode reflected in the other, the black-body temperature and the reflectivity can be simultaneously measured on the same surface.

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[1] At the Washington meeting of the American Physical Society, April 24, 1915, Dr. Hyde gave the effective wave length of transmission of the red glass screen, *a*, as 0.664 μ.

The first of these methods gave for solid tungsten an emissivity of 0.46 (for $\lambda = 0.667\ \mu$) and an average melting-point of 3532° K.

The second method gave as the emissivity of molten tungsten 0.425 (for $\lambda = .667\ \mu$) and a melting-point of 3566° K.

From a consideration of the sources of error involved in the determination, it is concluded that the most probable value for the melting-point of tungsten is 3540° K. ± 30°.

The writer wishes to express his indebtedness to Dr. W. E. Forsythe for his help in the calibration of the pyrometer, and to both Dr. Forsythe and Prof. C. E. Mendenhall for valuable suggestions as to the use and construction of the pyrometer. He also wishes to express his appreciation of the valuable coöperation and assistance in all the experimental work rendered by Mr. G. M. J. Mackay and Mr. C. V. Ferguson.

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THE CATHODE FALL IN GASES.[1]

By C. A. Skinner.

Each column of potentials in the tables (III, IV and V) was obtained with fresh gas at approximately the pressure indicated at its head—the current density always being accurately maintained at the value indicated at the top of the table.

At lower gas pressures the potentials begin to diverge distinctly from the fairly constant values found here. At higher gas pressures the mean free path of the electron is too small to allow of reliable measurements being made with a probe wire of practical size.

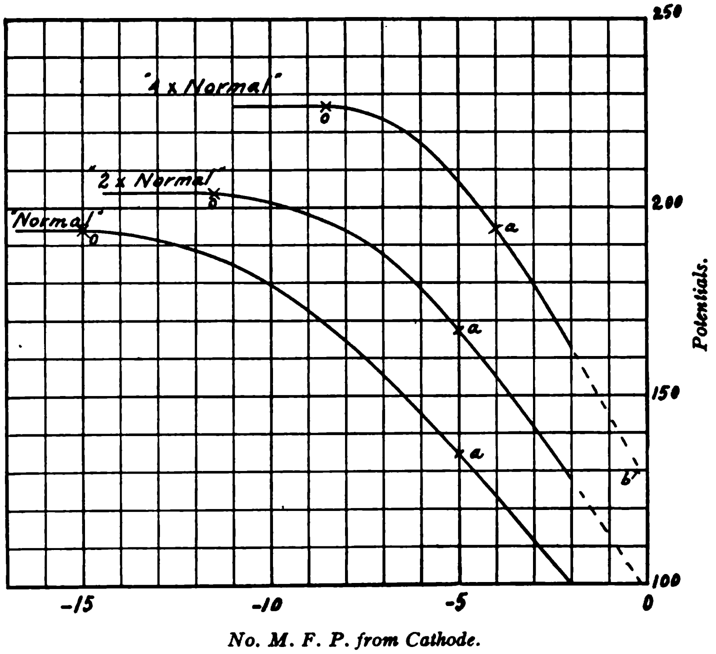

Fig. 1. Potential Curves in Hydrogen.

On comparing the individual values, given by the various gas pressures, with their means (column 7) we feel justified in concluding that over the range of pressures giving a constant value for the normal cathode fall,

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[1] Concluded from the June number, Vol. V, p. 496.

the potential at a given number of mean free paths from the cathode is simply a function of $(\bar{j}\lambda^2)$. That is, it is a function of the ratio of the current density to the square of the gas pressure.

The means in columns 7 are plotted as curves in Fig. 1. These potential curves show the interesting fact that the potential gradient approaches a constant maximum value as it nears the cathode.[1] This brings out a distinct similarity in the form of the gradient on the two sides of the negative glow—rising gradually as it does to a constant value in the unstriated positive column.

Test of the Theory by the Potential Curves.—From the expressions in (18) (l. c., p. 488) we may write for any point x_1, having a potential V_1,

$$\begin{aligned} V_0 - V_1 &< \left\{ K^{2/3}(\bar{j}\lambda^2)^{1/3}\left(\frac{x_1 - x_0}{\bar{\lambda}}\right)\right\}^{3/2} \\ &> \left\{ K^{2/3}(\bar{j}\lambda^2)^{1/3}\left(\frac{x_1 - x_0}{\bar{\lambda}}\right) - \epsilon^{2/3}\right\}^{3/2} + \epsilon \end{aligned} \tag{24}$$

from which

$$\begin{aligned} K &> \frac{1}{(\bar{j}\lambda^2)^{1/2}} \cdot \frac{(V_0 - V_1)}{\left(\frac{x_1 - x_0}{\bar{\lambda}}\right)^{3/2}} \\ &< \frac{1}{(\bar{j}\lambda^2)^{1/2}} \cdot \left\{ \frac{(V_0 - V_1 - \epsilon)^{2/3} + \epsilon^{2/3}}{\left(\frac{x_1 - x_0}{\bar{\lambda}}\right)} \right\}^{3/2}. \end{aligned} \tag{25}$$

The values for these upper and lower limits of K were calculated by substituting from the means of Tables III., IV. and V. the values at 2 m.f.p. the locations of x_0 being obtained from the curves of Fig. 1. The magnitudes thus obtained for K were

	"Normal."	2 × "Normal."	4 × "Normal."
Lower limit of K	10.3	9.5	9.8
Upper limit of K	12.8	12.1	12.8

These agree in indicating, as expected, that K does not change with current density.

Their mean value 11.5 was assumed as the correct magnitude, and therefrom the two limiting potential values calculated for each current

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[1] This is very different from the impression one gets from using the much less reliable method of measuring the gradient with two parallel wires, usually several mean free paths apart. One then is led to indicate the gradient as a continuous curve rising to a very large magnitude in front of the cathode.

TABLE III.

Potential Difference between Cathode and Points in the Gas at a Given Number of Mean Free Paths from it. For Normal Current Density: ($j\bar{\lambda}^2 = .038$).

No. of m. f. p.	Gas Pressures.					Means.
	1.1 mm.	1.6 mm.	2 mm.	2.5 mm.	3 mm.	
2	101 volts	99.5	98	101.5	98	99.5
3	114.5	114	112.5	111	109.5	112
4	128	127.5	121.5	125	120	123
5	141.5	142	134.5	135	127	136
7	165	164	154.5	155.5	145	155
9	181.5	181	171	167	163	173
11	191	187	183	177	176.5	183
15	200	196.5	193	189	192	194

TABLE IV.

Potential Difference between Cathode and Points in the Gas at a Given Number of Mean Free Paths from it. For Twice Normal Current Density: ($j\bar{\lambda}^2 = .076$).

No. of m. f. p.	Gas Pressures.					Means.
	1.1 mm.	1.6 mm.	2 mm.	2.5 mm.	3 mm.	
2	120 volts	130	124	131	130	127
3	138.5	145	141.5	144	144.5	143
4	154.5	161	152	157	157	156
5	170	—	—	165	—	167
6	—	185	177	177	172	178
7	191	—	—	184	—	187
8	—	198	193	192.5	190	193
9	203					
10		203	201	198	200	200
12	207	204.5	203	201	205.5	204

TABLE V.

Potential Difference between Cathode and Points in the Gas at a Given Number of Mean Free Paths from it. For Four Times Normal Current Density: ($j\bar{\lambda}^2 = .152$).

No. of m. f. p.	Gas Pressures.					Means.
	1.1 mm.	1.6 mm.	2 mm.	2.5 mm.	3 mm.	
2	149.5 volts	160	162.5	168	174	163
3	173	177	180	184	186	180
4	191	195	192.5	198	202	196
5	205.5	208	—	206	—	206
6	—	—	218	—	216	217
7	224	223	—	221	—	223
10	226	225	229	222	232	227

density by substitution in their respective expressions on the right hand side of (24). The observed potentials at two mean free paths from the cathode were used in each case as the starting point, and the number of mean free paths from the cathode to the negative glow (point of zero gradient) were obtained from the curves of Fig. 1.

Table VI.

Comparison of Calculated with Observed Potentials.

Dist. from Cath. (m. f. p.)	"Normal" Current Density.			"Twice-Normal" Current Density.			"Four-Normal" Current Density.		
	Calc.	Limits.	Obs.	Calc.	Limits.	Obs.	Calc.	Limits.	Obs.
.2	77	78	—	100	102	—	129	131	—
1	88	88	—	112	113	—	146	146	—
2	100	100	100	127	127	127	163	163	163
3	112	109	112	142	139	143	179	177	180
4	123	119	123	155	150	156	194	189	196
5	134	128	136	167	161	167	208	199	206
6	144	136	—	179	170	178	220	206	217
7	154	144	155	190	178	187	229	—	223
8	164	152	—	199	184	193	—	—	—
8.5	—	—	—	—	—	—	238	219	227
9	172	158	173	207	—	—			
10	180	163	—	214	—	200			
11	187	168	183	—	—	—			
11.5	—	—	—	220	199	204			
12	193	169							
13	199	—							
14	203	—							
15	205	181	194						

These theoretical values are given in Table VI. along with the corresponding observed magnitudes—the means of Tables III., IV. and V. The observed values, with very slight exceptions, are consistent with the calculated limits.

Mobility of the Positive Ions.—The quantity K will obviously serve for calculating $\overset{+}{\mu}$, the mobility of the positive ions. As used in (17)—l. c., p. 488—this mobility is defined as the velocity of the ions in unit electrostatic field. In calculating the above value of K the potentials were measured in volts, the current in milliamperes, and the mean free path of the electrons in millimeters. The theory is developed however with the c.g.s.e.s. system of units as a basis. Using this system for the electrical units and $\bar{\lambda}$ in centimeters we obtain for the corresponding values of K.

	In Practical Units.	In c.g.s.e.s. Units.
Mean of lower limits of K..........	9.9	2×10^{-4}
Mean of upper limits of K............	12.6	2.4×10^{-4}
K as used..........................	11.5	2.2×10^{-4}

Using the c.g.s.e.s. values for K it follows from (17), (17*a*) and (24) that

$$\overset{+}{\mu} = \frac{16\pi\bar{\lambda}}{9K^2}.$$

This gives for a gas pressure of one millimeter ($\bar{\lambda} = .072$ cm.) the values of $\overset{+}{\mu}$ corresponding with those of K in the preceding table.

	In Unit Electrostatic Field.	In Field of One Volt per Cm.
Lower limit of $\overset{+}{\mu}$	6.7×10^6 cm./sec.	2.2×10^4 cm./sec.
Upper limit of $\overset{+}{\mu}$	10.8×10^6	3.6×10^4
Mean ($K = 2.2 \times 10^{-4}$)	8.2×10^6	2.7×10^4

These values of $\overset{+}{\mu}$ are about six times the magnitude as customarily obtained, with, however, very much smaller potential gradients per mean free path.[1]

There is no doubt that the mobility of the electrons increases at low pressures much more rapidly than their mean free path. The above is however the first experimental evidence that the same occurs with the positive ions.

If we take into account the velocity as imparted by the field between collisions the high value for the mobility given here does not appear unreasonably large. The field strengths under which the above measurements were made run up to 2 and 3 volts per mean free path of the positive ion—or molecule. To a freely accelerated molecule of hydrogen with univalent charge, potentials of these magnitudes would impart velocities respectively of 1.4×10^6 cm./sec. and 1.7×10^6 cm./sec. The square root of the mean square velocity of the hydrogen molecules at ordinary temperature is about 1.7×10^5 cm./sec., or only one-eighth to one-tenth the accelerated velocity imparted between collisions (the ion considered as starting from rest after each collision). Where the accelerated velocity of the ion is larger than the temperature velocity of the molecules, we should expect a relatively larger mobility than where it is small compared with the temperature velocity—as has been the case with previous measurements.

Test of the Theory of Rebound.—From the fact that the difference of potential between the cathode and any definite number of mean free paths distance from it is simply a function of ($j\bar{\lambda}^2$) it follows that the immediate fall at the cathode is also simply a function of the same quantity—it being assumed to be over a distance of one m.f.p. of the positive ion—or molecule. This requires that the factor P in (22) and (23)—l. c., pp. 492, 493—be either *constant* with varying current, or, that it be a *function also of* $(\bar{j}\lambda^2)$. If it is a constant (22) requires the fall over the region of rebound to be proportional to $(\bar{j}\lambda^2)^{2/3}$. The theoretical values in table VI agree closely in fixing the values of V_b (at .2 m.f.p. of the electron from the cathode) for the different current densities. The following table taken from these serves to show up the nature of P.

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[1] From the value given in Winklemann for atm. pressure that at one mm. should be 4.3×10^3 cm./sec. with one volt per cm.

V_b	Ratios.	$(\bar{j}\lambda^2)^{\frac{2}{3}}$	Ratios.	$(\bar{j}\lambda^2)^{.38}$	Ratios.
77	1	.113	1	.289	1
101	1.31	.180	1.59	.375	1.30
130	1.69	.285	2.53	.488	1.69

These prove distinctly that V_b is not proportional to $(\bar{j}\lambda^2)^{2/3}$, but instead is, for the few current densities used, very closely proportional to $(\bar{j}\lambda^2)^{.38}$, which requires that P *decrease* with increasing V_b. The theory, as already stated, requires it to *increase*.

Magnitude of the Electron Current from the Cathode.—From equations (4) and (8)—l. c., p. 486—the ratio of the electron current leaving the cathode j_k to the total current $\bar{j}$ may be derived.

$$\frac{\bar{j}_k}{\bar{j}} = \frac{\bar{\mu}}{\bar{\mu} + \overset{+}{\mu}} \cdot 2^{-\left\{\frac{x_k - x_a}{\bar{\lambda}} + \frac{V_0 - V_a}{\epsilon}\right\}}.$$

Where $\bar{\mu}$ and $\overset{+}{\mu}$ are the mobilities in the very low gradient region of the negative glow, $[(x_k - x_a)/\lambda]$ the number of m.f.p. from the cathode to where the potential gradient per m.f.p. drops below ϵ, and $(V_0 - V_a)$ the fall of potential between this point and the negative glow.

The following table gives these magnitudes as obtained from the curves in Fig. 1. It may be noted that an error in locating x_a has no appreciable effect on the result; also, that $\bar{\mu}$ and $\overset{+}{\mu}$ being assumed to have the same value does not affect the results as much as the natural errors in the exponential quantities.

Current Density.	$\left(\frac{x_k - x_a}{\bar{\lambda}}\right)$	$\left(\frac{V_0 - V_a}{\epsilon}\right)$	$\left(\frac{\bar{j}_k}{\bar{j}}\right)$ Calc.
"Normal"..............	5	5.3	4×10^{-4}
2 × "Normal"..........	5	3.4	15×10^{-4}
4 × "Normal"..........	4	2.9	42×10^{-4}

These results are enlightening in that they show, under the theory here advanced, what an extremely small part of the current is furnished by the initial ionizing agency.[1]

The foregoing table shows too that the ratio of electron emission to the current density increases with the latter. It is interesting to know to what magnitudes this ratio may rise. We have carefully measured the extent of the cathode dark space in hydrogen and found that it remains constant—about 6.5 m.f.p. from the cathode—over an extreme range of current densities. As the current density increases, the point of zero gradient approaches closer and closer to the edge of this dark space but never quite reaches it. This suggests, that with the highest current densities (there being a correspondingly abrupt rise in the potential gradient from its zero value in the negative glow) the number of ionizations between cathode and negative glow could not drop much below *six*—giving an upper limit of about .01 for $(\bar{j}_k/j)$.

In nitrogen, on the other hand, the cathode dark space decreases considerably with increasing current density—*e. g.*, with a pressure as low as 2 mm. it can, by increasing the current, be made to almost disappear. This suggests that $(\bar{j}_k/j)$ may rise to a distinctly larger magnitude in nitrogen than in hydrogen.

Explanation of the "Normal" Cathode Fall.—The curves of Fig. 1 and calculated values in Table VI. both show that while the immediate fall at the cathode increases with the current density, the fall over the rest of the distance to the negative glow decreases. This decrease in the gas arises from the increased ratio of the electron current from the cathode to the total current, which, by the relative increase in ionization it produces, reduces the distance to the point of minimum gradient.

Conversely then, as the current density is decreased, a certain point should be reached where the rate of *decrease* in the immediate cathode fall is just balanced by the rate of *increase* in the rest of the cathode fall. At that current density the cathode fall would be a minimum.

An experimental verification of this view was incidentally obtained with an aluminium cathode in hydrogen at a pressure of .5 mm. The normal current density was sought by starting at a higher value then gradually reducing the current and simultaneously observing the cathode fall. This latter dropped to a magnitude of about 232 volts, then rose again with a further reduction of the current—being carried to a value of about 240 volts without the luminosity on the cathode indicating an uneven distribution of the current over its face. The observations were repeated with the same result. The current density at which this minimum cathode fall was observed proved to be of the same magnitude as the normal current density obtained at higher gas pressures.

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[1] The above results refer of course to an aluminium cathode. With a steel cathode in hydrogen, and normal current density $(\bar{j}_k/j)$ comes to about 5×10^{-5}—which is only one eighth the ratio for aluminium. This is consistent with the well known fact that aluminium is a much more copious source of cathode rays than the heavier metals.

We may conclude therefore that the " normal " cathode current density is that giving a minimum cathode fall, which condition (neglecting small effects beyond the negative glow) corresponds to a minimum loss of electrical energy in sending a given current through the gas.

Similar conclusions may be drawn from (23)—l. c., p. 493—by enquiring under what current densities the expressions on the right hand side have a minimum value. Inasmuch however, as this enquiry cannot be made to result in quantitative results, at present at least, it does not appear wise to burden this article with the discussion.

I wish to express my indebtedness to Dr. A. Q. Tool for his assistance in the experimental work and also for valuable suggestions on the theoretical part.

The Brace Laboratory of Physics,
University of Nebraska,
February, 1915.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

ON X-RAY WAVE-LENGTHS.[1]

BY WILLIAM DUANE AND FRANKLIN L. HUNT.

AT its Philadelphia meeting (December, 1914) one of us presented a paper to this Society describing experiments on the relation between the wave-lengths of X-Rays and the voltages required to produce them. The X-Rays came from the tungsten target in one of the tubes designed by W. D. Coolidge,[2] and belonged to the general or "white light" X-radiation and not to the characteristic X-radiation. The generator supplying current to the tube produced a *roughly* constant difference of potential, which was measured by means of the voltmeter attached to the generator and also by means of the length of sparks between two metal balls each 2 cm. in diameter. This gave, of course, only an approximate estimate of the voltage. The wave-length λ_e was calculated from measurements of the mass-coefficient of absorption μ/ρ of the X-rays in aluminium, the formula being

$$\frac{\mu}{\rho} = 14.9\,\lambda_e^3 \quad (\lambda_e \text{ expressed in ångströms}).$$

This method gives what may be called the *effective* wave-length of the X-rays. With $V = 43{,}000$ volts difference of potential between the electrodes of the tube the effective wave-length of the X-rays after they had passed through 2 mm. of aluminium was found to be $\lambda_e = .45$ ångström. Calling the ratio of the energy of a cathode-ray particle to the effective frequency of the X-rays h_e, this gives $h_e = 10 \times 10^{-27}$, a quantity of the order of magnitude, but somewhat greater than Planck's radiation constant $h = 6.41 \times 10^{-27}$.

The authors of this paper have repeated the experiments using a high tension storage battery to supply current through the tube. The difference of potential between the electrodes of the tube was measured by means of an excellent electrostatic voltmeter designed by Dr. E. L. Chaffee. We calibrated this instrument by measuring the current flowing from the storage battery through a number of manganin wire coils of known resistance. The total resistance of the coils joined in series amounted to about one million ohms. The measurements appear to be thoroughly reliable.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] PHYSICAL REVIEW, December, 1913.

On plotting the logarithm of the intensity of the X-rays produced by a given difference of potential against the total mass per square centimeter of the aluminium plates through which the rays had passed, we obtained a line that was somewhat curved near the intensity axis, but which became nearly straight at a short distance from it (Fig. 1). This means that both the coefficient of absorption and the effective wave-length of the X-rays decrease as the rays pass through matter. In other words a *constant* difference of potential such as that of a storage battery does not produce *homogeneous* X-rays. The coefficient of absorption and effective wave-length, however, vary very little after the rays have passed through several millimeters of aluminium.

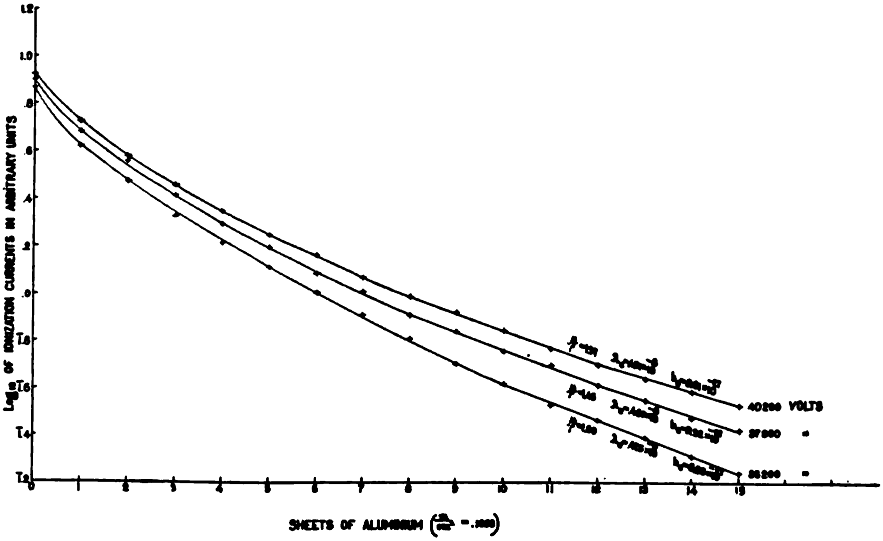

Fig. 1.

The following table contains the mass coefficients of absorption μ/ρ and the effective wave-lengths λ_e, frequencies γ_e and radiation constants h_e after the rays had passed through three millimeters of aluminium for voltages in the neighborhood of 35,000–40,000 volts.

Voltage.	Coefficient of Absorption, μ/ρ.	Effective Wave-Length, λ_e.	Effective Frequency, ν_e.	Effective Radiation Constant, h_e.
35,200	1.60	$.475 \times 10^{-8}$	6.32×10^{18}	8.85×10^{-27}
37,900	1.45	$.460 \times 10^{-8}$	6.52×10^{18}	9.22×10^{-27}
40,200	1.37	$.451 \times 10^{-8}$	6.65×10^{18}	9.61×10^{-27}

The value of h_e is in good agreement with that previously reported. It increases slightly as the voltage rises.

As stated above a constant voltage applied to a tube does not produce X-rays of a single wave-length; and we therefore set ourselves the problem of determining the minimum wave-length that can be produced by a given difference of potential. For this purpose we used an X-ray spectrometer, kindly loaned to us by Dr. D. L. Webster. The X-rays were reflected from the 100 planes of calcite ($CaCO_3$) into a small ionization chamber containing air and ethylbromide (C_2H_5Br). The formula

$$\lambda = 2a \sin \theta$$

gives the wave-length, where θ is the glancing angle of reflection, and $a = 3.04 \times 10^{-8}$ according to Bragg.

Two methods of procedure are open to us: either we may maintain the voltage at a constant value and measure the ionization currents due to the X-rays reflected at different angles, or we may set the spectrometer for a given angle and change the voltage. The latter appears to be the better method, for

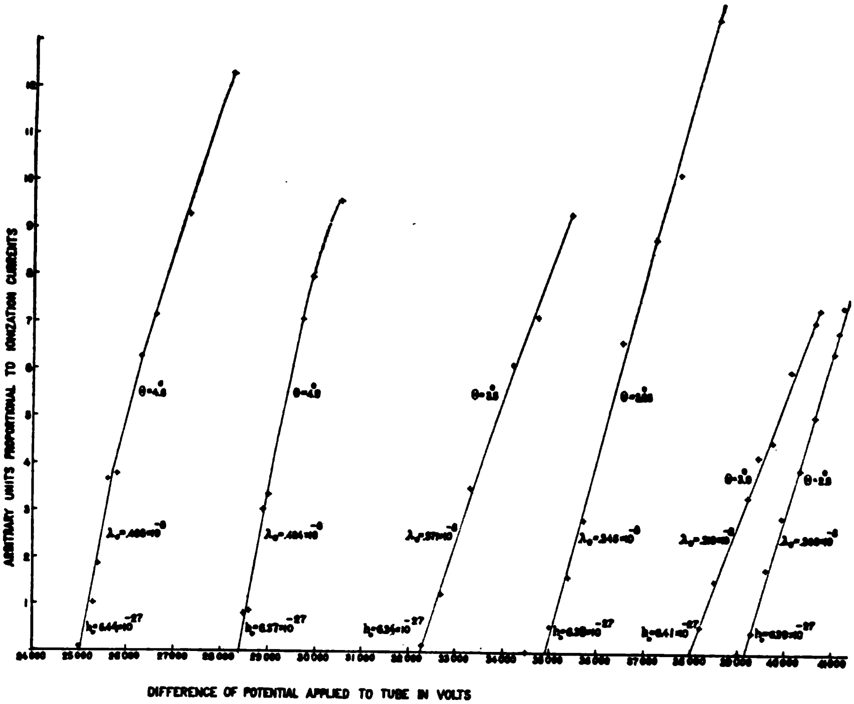

Fig. 2.

the ionization currents vary in a complicated way with the coefficients of absorption in the crystal and ethylbromide, etc., and with the coefficient of reflection from the crystal, and all of these coefficients vary with the wave-length and glancing angle.

We have made six series of measurements at six different glancing angles corresponding respectively to six different wave-lengths. The quantities measured were the voltage applied to the tube, the ionization current and the current passing through the tube. The last furnished a correction to be applied to the ionization current, for, other things being the same, the two currents are approximately proportional to each other.

After correcting for variations in the current flowing through the tube and for the natural leak in the ionization chamber we plotted six curves (Fig. 2) each representing the ionization current as a function of the voltage for a constant wave-length. Near the axis of zero ionization currents the curves are almost straight and meet this axis at certain definite points making apparently finite angles (less than 90°) with it. These points represent in each case the minimum voltage V_0 required to produce X-rays of the corresponding wave-length λ_0. If the voltage is less than V_0 no rays of the given wave-length λ_0 are produced, but if the voltage exceeds V_0 X-rays of that wave-length are always produced, no matter how high the voltage rises within the limits of our battery, and there is no reason to suppose that higher voltages would not also produce them. Our results show that the minimum voltage V_0 required to produce X-rays of wave-length λ_0 is given by the energy equation

$$V_0e = h\nu_0 = \frac{hc}{\lambda_0},$$

where e = electron charge, c = velocity of light, and also that the energy radiated per second *at* this wave-length λ_0 is infinitely small.

The following table contains the experimental data and the values of h calculated from them.

V_0 (Volts).	θ_0	λ_0	ν_0	h
39,150	2.90	$.307 \times 10^{-8}$	9.77×10^{18}	6.39×10^{-27}
37,950	3.00	$.318 \times 10^{-8}$	9.44×10^{18}	6.41×10^{-27}
34,900	3.25	$.345 \times 10^{-8}$	8.69×10^{18}	6.38×10^{-27}
32,250	3.50	$.371 \times 10^{-8}$	8.08×10^{18}	6.34×10^{-27}
28,400	4.00	$.425 \times 10^{-8}$	7.06×10^{18}	6.37×10^{-27}
25,000	4.60	$.486 \times 10^{-8}$	6.18×10^{18}	6.44×10^{-27}

Corrections for the width of the slit and of the source of the rays amounting to an increase of $2'.5$ in the value of θ_0 have been added in calculating the values of h. The average value of h is $h = 6.39 \times 10^{-27}$, in very close agreement with the value given by Planck in the last edition of his book, namely 6.41×10^{-27}. We used an average value of $e = 4.71 \times 10^{-10}$ in calculating the energy of the cathode particles. Any error in estimating the grating constant a of the crystal enters, of course, into our measurement of λ_0. Our results furnish strong evidence in favor of the fundamental principle of the quantum hypothesis, for they show that rays of frequency ν are not produced unless the energy available equals $h\nu$, and also, incidentally, they prove the general correctness of W. L. Bragg's estimates of the distances between the atoms of crystals.

In attacking the problem by the other method mentioned above we kept the voltage as nearly constant as possible by adding cells to the battery as it gradually ran down, and measured the ionization currents with the spectrometer set for different angles corresponding to different X-ray wave-lengths. This work was done in collaboration with Dr. D. L. Webster. The curves (Fig. 3) representing the ionization currents (corrected as before for the natural leak of the ionization chamber and variations in the current through the tube) as a function of the wave-length at constant voltage show that no energy is radiated at wave-lengths shorter than λ_0 given by Planck's radiation constant. As the wave-length increases beyond λ_0 the ionization current rises, reaches a maximum and then rapidly falls. As stated above these ionization currents do not represent accurately the energy radiated. There can be no doubt, however, but that the energy radiated between the wave-lengths λ and $\lambda + d\lambda$ reaches a maximum value at some wave-length λ_m.

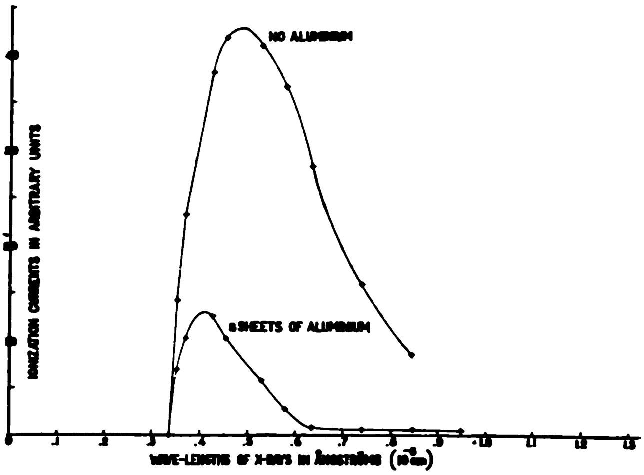

Fig. 3.

A second curve (Fig. 3) represents the X-radiation that has passed through 3 mm. of aluminium in addition to the walls of the tube as a function of the wave-length. The maximum in the curve is much lower than before and has shifted toward the smaller wave-lengths, without, however, changing the value of λ_0.

To sum up: a *constant* difference of potential applied to an X-ray tube produces X-rays of a great variety of wave-lengths. The radiation is not homogeneous. We recognize three important wave-lengths and corresponding frequencies associated with the constant voltage. (*a*) The maximum limit of the frequencies ν_0, which multiplied by Planck's radiation constant equals the energy of a cathode particle as given by the product of its charge into the constant voltage applied to the tube. The energy radiated per second between the frequencies ν_0 and $\nu_0 - d\nu$ is, however, an infinitesimal of higher order than $d\nu$, apparently of the second, if $d\nu$ is of the first order. (*b*) The effective wave-length λ_e and frequency ν_e, which are the wave-length and frequency of

X-rays having the same coefficient of absorption as the whole radiation. λ_e decreases and ν_e increases as the rays pass through matter. The ratio of λ_e to λ_0 and of ν_0 to ν_e is about 1.50 at 40,000 volts and after the rays have passed through 3 mm. of aluminium. This ratio increases as the voltage increases and consequently the effective frequency is not proportional to the voltage. It increases less rapidly than the voltage. (*c*) The wave-length λ_m and frequency ν_m corresponding to the maximum energy radiation. These we have not yet determined accurately.

We have found no evidence that an appreciable number of electrical vibrators in the target store up energy from two or more cathode particles and then radiate it in the form of a quantum $h\nu$ of frequency higher than that corresponding to the energy of any one of them.

Harvard University,
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Magnetization by Rotation.[1]

By S. J. Barnett.

1. On the electron theory it is shown[2] that by a sort of molecular gyroscopic action a body of any magnetic substance becomes magnetized when set into rotation, the intrinsic magnetic intensity being uniform, parallel to the axis of rotation, proportional to the angular velocity, and (like the magnetization of the earth) directed oppositely to the intensity which would be produced by an electric current circulating around the body in the direction of rotation. It is shown further that a non-magnetic substance does not become magnetized. The theory of the converse effect is developed in a very simple manner. An experimental investigation of this effect is now in progress.

2. There is described a series of experiments, beginning in 1909, on the magnetization of iron rods by rotation. After the elimination of all suspected sources of systematic error there has been found and measured at different speeds an effect precisely similar to that required by the above theory, and inexplicable on any other theory hitherto proposed. The method of electromagnetic induction was used, a fluxmeter whose deflections were read to 0.1 mm. at the scale distance 8 m. being the chief measuring instrument. The intrinsic magnetic intensity of rotation, and the change of flux-density, per unit speed were found to be $3.1 \times 10^{-7} \frac{\text{gauss}}{\text{r.p.s.}}$ and $1.9 \times 10^{-5}\left(\frac{\text{maxwell}}{\text{cm.}^2}\right)$ per r.p.s., respectively. Experiments made for a different purpose by Lebedew[3] in 1912 show that this effect does not exist in the five non-magnetic substances investigated.

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[1] Abstract of papers presented to the American Physical Society in December, 1914, and April, 1915.

[2] See also S. J. Barnett, Science, 30, 1909, p. 413, and A. Schuster, Proc. Phys. Soc. London, 24, 1911–12, p. 121.

[3] P. Lebedew, Ann. d. Phys., 39, 1912, p. 840.

3. Together with the change of (residual) flux proportional to the angular velocity, another change proportional to its square has been found and proved to be due to the radial expansion of the rod produced by the rotation.

4. The intensity of magnetization produced in the rotating iron per unit speed was about 1.5×10^{-6} c.g.s. unit per r.p.s. If the rod had been rotated at the speed of the earth its intensity of magnetization would have been about 2×10^{-10} that of the earth, and still less if the form had been spherical. This, however, does not prove that the earth's magnetization is not produced by the effect in question, as we are entirely ignorant of the magnetic properties of all substances under the conditions prevailing within almost the whole of the earth. Other causes are mentioned as probably accounting for at least part of the earth's magnetism. Schuster has pointed out that an effect of the kind investigated here may explain the secular variation as well as the mean magnetization of the earth.

5. Experiments, incidental to the work, on the use of a fluxmeter when direct and alternating flux changes occur separately or superposed are described.

OHIO STATE UNIVERSITY,
June, 1915.

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THE

PHYSICAL REVIEW.

THE BALLISTIC USE OF A MOVING-COIL GALAVANOMETER IN MEASURING DISCHARGES OBEYING THE EXPONENTIAL DECAY LAW.

By A. G. Worthing.

Introduction.

In the ballistic use of galvanometers, it is generally assumed that the period of discharge must be negligible compared with the period of the galvanometer. That this assumption is not necessary does not seem to be well known.

Weber[1] seems to have first considered and obtained an approximate solution for the effect on galvanometer throws due to the duration of the rotation of an earth-inductor producing them. Chwolson[2] later considered in the multiplication and the recoil methods, the effects of errors in the timing of the successive throws. According to Dorn,[3] Chwolson's work was in error. Dorn himself developed approximation formulas for the effects of these two deviations from simple theory and verified them for the case of the sine discharge of the earth-inductor. Diesselhorst[4] revised in a simpler way the work of Dorn, and in addition considered for discharges of short duration the limits of error due to variations in the law of the unidirectional discharge, the correction factor for a constant current discharge, and the first order correction for a damped discharge. More recently Peirce,[5] in an excellent article, using a graphical method considered the effects of the duration of discharge for discharges of various types, and also deduced from theoretical considerations the correction factor to be applied to the galvanometer throws for certain simple types, among which was that obeying the exponential decay law. Unfortunately the papers of both Diesselhorst and Peirce are subject, as will be noted later, to a misinterpretation. Moreover the paper by Peirce, though it represents a distinct advance over previous work, is still incomplete.

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[1] Abh. der k. Sachs. Ges. d. Wiss., 1, p. 230, 1846.

[2] Melanges physiques et chimiques, St. Petersburg, p. 403, 1881.

[3] Ann. d. Phys., N. F., 17, p. 654, 1882.

[4] Ann. d. Phys., 4 F., 9, p. 712, 1902.

[5] Proc. of Am. Acad. of Arts and Sci., 44, p. 283, 1909.

Grassot[1] in connection with his fluxmeter described a method of measuring quantities of electricity which is practically independent of the duration or manner of passage. The same principle, that of a relatively very weak coil control, was used and the same practical results were obtained by Rohmann[2] in his second method of increasing the sensibility of a moving-coil galvanometer by means of large variations in the strength of the magnetic field containing the moving coil.

H. A. Wilson[3] considered the case of an undamped moving-coil galvanometer with a so-called radial field and concluded that, even though the time of passage of the transient current was not small compared with the galvanometer period, the deflections would be proportional to the quantities passing. The consideration of a steady current deflection shows the conclusion to be in error. Wenner,[4] considering the charging of a condenser through an undamped galvanometer, concluded that, within certain limits, the deflections were independent of the rate of charging.

The writer's special interest in this general subject of measuring discharges of considerable duration has resulted from an attempt to apply Corbino's[5] method in checking some results obtained on the thermal capacity of tungsten at incandescent temperatures. It was soon noted that the common assumption of a period of discharge negligible in comparison with the period of the galvanometer was far from the truth. In ignorance of the works of Dorn, Diesselhorst, and Peirce, it seemed to the writer that a definite correction factor, when once the law of discharge is known, should be obtainable. For the case of the exponentially decaying discharge, the one of immediate interest, such a simple factor has been found. A certain lack of definiteness and completeness, as already suggested, in the previous discussions of this case has led to the presentation of the following statement of theory and its test.

THEORY.

The equation of motion for a galvanometer coil traversed by a current I (see Table I.) and located centrally in a so-called radial field—that is

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[1] Jour. de Phys., IV., 3, p. 696, 1904. See also Jones, Proc. of Phys. Soc. of Lond., 26, p. 80, 1914.

[2] Phys. Zeit., 14, p. 203, 1913.

[3] Phil. Mag., VI., 12, p. 269, 1906.

[4] PHYS. REV., 25, p. 139, 1907.

[5] Phys. Zeit., 13, p. 375, 1912.

Table I.

Symbols and Quantities.

I	Current traversing the galvanometer coil.
θ	Angular deflection of coil.
t	Time.
K	Moment of inertia of coil.
B	Damping factor for the coil on open circuit.
B_1	Damping factor for the coil on closed circuit.
D	Restoring couple per unit angular deflection due to the coil suspension.
G	Deflecting couple per unit of current traversing the coil.
E	Intrinsic E. M. F. in the circuit containing the coil.
r	Resistance of the circuit containing the coil.
L	Self inductance of the circuit containing the coil.
Q	Quantity of electricity discharged through the coil.
E_0	Initial value of E.
p	Inverse of the time-constant for the discharge through the coil.
$c_1, c_2, c_3, \beta_1, \beta_2, \gamma, \omega, p_1$	Constants defined by equations (9), (10), (11), (12), (28), (29) and (38).
θ_0	Maximum value of θ.
τ	Value of t corresponding to θ_0.
T	Period of galvanometer for an impulsive discharge.
λ	Logarithmic decrement of galvanometer for an impulsive discharge.
ϕ	Correction factor giving ratio of deflection for an impulsive discharge to the deflection for a prolonged discharge of the same quantity.
(′)	Quantities referring to an impulsive closed circuit discharge as through the secondary of a mutual-inductance.
(″)	Quantities referring to an impulsive open circuit discharge as from a condenser.

one in which for all ordinary deflections of the coil the torque due to a current is independent of the position of the coil—is given by

$$GI - K\frac{d^2\theta}{dt^2} - B\frac{d\theta}{dt} - D\theta = 0. \tag{1}$$

The successive terms represent torques due respectively to the current through the coil, the inertia of the moving system, the damping from other causes than the generator action of the coil, and the directing action of the suspension. Attention should here be directed to the fact that the damping effect due to the generator action of the coil is included in the torque GI, for the current I which actually flows is, on account of the generator action, less than that current which would flow in case there were no such action, that is in case the coil were held rigid. In other words, the damping effect due to the generator action is manifested by a reduced current, I. In general, neglecting capacity effects, an expression for I may be obtained by considering the E.M.F.'s of the galvanometer coil circuit, thus

$$E - L\frac{dI}{dt} - rI - G\frac{d\theta}{dt} = 0. \tag{2}$$

Therefore with a slight rearrangement we have

$$(3)\qquad \frac{d^2\theta}{dt^2}+\frac{B+G^2/r}{K}\frac{d\theta}{dt}+\frac{D}{K}\theta=\frac{G}{Kr}\left(E-L\frac{dI}{dt}\right).$$

As is well known no counter E.M.F. other than that indicated in (2) by rI can affect the total quantity of electricity discharged through the galvanometer, due account being taken of the sign of the discharge at various stages. Thus

$$(4)\quad Q=\int_0^\infty I\,dt=\int_0^\infty\frac{E}{r}dt-\frac{L}{r}\int_0^\infty\frac{dI}{dt}dt-\frac{G}{r}\int_0^\infty\frac{d\theta}{dt}dt=\int_0^\infty\frac{E}{r}dt,$$

that is, the total charge which passes depends on the E.M.F. and the resistance only. Differentiation of (1) with respect to time leads to an expression for dI/dt which may be substituted in (3). This gives

$$(5)\quad \frac{d^3\theta}{dt^3}+\frac{LB+Kr}{LK}\frac{d^2\theta}{dt^2}+\frac{LD+G^2+Br}{LK}\frac{d\theta}{dt}+\frac{Dr}{LK}\theta=\frac{G}{LK}E.$$

For our special problem it is necessary to define what is meant by a "discharge obeying the exponential decay law." The most practical definition requires that, for such a discharge, there be present in the circuit an intrinsic E.M.F. of the form

$$(6)\qquad E=E_0e^{-pt}.$$

The discharge current, however, which exists in a galvanometer circuit, on account of the distorting effect of the generator action of the moving coil, will seldom be found to obey a similar law. In case the term $G(d\theta/dt)$ of (2) is sufficiently small comparatively, there is a close approach to it. This condition occurs commonly during a considerable portion of the discharge in case (6) is fulfilled, only when $1/p$ is large in comparison with the time of throw of the galvanometer. The treatment of such cases is not important since it has been long known that the galvanometer deflection then tends towards independence of the particular law of discharge and towards dependence only upon the quantity of electricity passing.

Our particular interest, however, is in measuring discharges where $1/p$ is of the order of the time of throw of the galvanometer, that is in obtaining by means of a correction factor the throw in case the whole quantity had passed in a very short period of time. In the process of carrying out this plan (5) may be actually solved subject to (6) by a method similar to that used below for the simpler case in which the self-inductance is neglected. Computation shows, as will be pointed out later, that for the writer's tests and also for most other probable tests such a procedure is justifiable. With this assumption of a negligible self-inductance, there results from either (3) or (5)

(7) $$\frac{d^2\theta}{dt^2} + \frac{B + G^2/r}{K}\frac{d\theta}{dt} + \frac{D}{K}\theta = \frac{GE_0}{Kr}e^{-pt}.$$

By means of (4), E_0/r may be replaced by Qp. (7) may then be written as

(8) $$\frac{d^2\theta}{dt^2} + \frac{B_1}{K}\frac{d\theta}{dt} + \frac{D}{K}\theta = \frac{GQp}{K}e^{-pt}.$$

It is to be noticed by comparing (8) and (1) that when the self-inductance effect is negligible, the behavior of the coil when in a closed circuit containing an intrinsic E.M.F. obeying (6), is exactly the same as though it possessed a new damping coefficient B_1 instead of B and were traversed by a current rigidly obeying the exponential decay law. The misinterpretation liable to follow in considering the works of Diesselhorst and Peirce, as mentioned above, consists in relating B_1 to the actual current flowing through the galvanometer coil. If one considers theoretically the form of the current curve existing in a galvanometer circuit as it would exist but for the generator action of the coil, he is not liable to error. The case is quite different, however, if one determines with an oscillograph the actual current curve.

The complete solution of (8) is of the form

(9) $$\theta = c_1e^{-\beta_1 t} + c_2e^{-\beta_2 t} + c_3e^{-pt},$$

where

(10) $$\beta_1 = \frac{1}{2K}\left(B_1 + \sqrt{B_1^2 - 4KD}\right),$$

(11) $$\beta_2 = \frac{1}{2K}\left(B_1 - \sqrt{B_1^2 - 4KD}\right),$$

and

(12) $$c_3 = \frac{GQp}{K(p - \beta_1)(p - \beta_2)}.$$

Introducing the natural boundary conditions

(13) $$[\theta = 0]_{t=0} \quad \text{and} \quad \left[\frac{d\theta}{dt} = 0\right]_{t=0},$$

gives

(14) $$\frac{\theta}{c_3} = \frac{p - \beta_2}{\beta_2 - \beta_1}e^{-\beta_1 t} + \frac{p - \beta_1}{\beta_1 - \beta_2}e^{-\beta_2 t} + e^{-pt}.$$

Differentiation of (14) leads to

(15) $$\frac{1}{pc_3}\frac{d\theta}{dt} = \frac{p - \beta_2}{\beta_1 - \beta_2}\times\frac{\beta_1}{p}e^{-\beta_1 t} + \frac{p - \beta_1}{\beta_2 - \beta_1}\times\frac{\beta_2}{p}e^{-\beta_2 t} - e^{-pt}.$$

To obtain an expression for the maximum angular deflection θ_0, at time τ, (14) and (15) may be combined subject to

$$\left[\frac{d\theta}{dt} = 0\right]_{t=\tau}. \tag{16}$$

We then have on substituting the value for c_3 from (12)

$$\theta_0 = \frac{GQ}{K(\beta_2 - \beta_1)}(e^{-\beta_1\tau} - e^{-\beta_2\tau}). \tag{17}$$

As is usual in similar cases dealing with a damped moving coil actuated by an impulsive discharge, we must consider three cases depending on whether the term $(B_1^2 - 4KD)$ common to the expressions for β_1 and β_2 is less than, equal to, or greater than zero.

Condition I. $(B_1^2 - 4KD) < 0$.

β_1 and β_2 are independent of the characteristics of the discharge, being thus the same as for the case of an impulsive discharge. A negative value of the radical part of β_1 and β_2 leads us to expect here as in the simpler case some sort of a damped vibrating action. In order to introduce the characteristics of the motion accompanying the impulsive discharge let us as in that simpler case write

$$\beta_1 = \frac{2}{T}(\lambda + \pi\sqrt{-1}) \tag{18}$$

and

$$\beta_2 = \frac{2}{T}(\lambda - \pi\sqrt{-1}). \tag{19}$$

T and λ represent respectively the period and the logarithmic decrement of the motion in the simpler case. Substitution of (18) and (19) in (17) gives

$$\theta_0 = \frac{GQT}{2\pi K}e^{-2\lambda(\tau/T)}\sin 2\pi\frac{\tau}{T}. \tag{20}$$

The value of τ is determined by applying condition (16) to (15). There results when β_1 and β_2 are eliminated,

$$e^{-[p-(2\lambda/T)]\tau} = \cos\frac{2\pi}{T}\tau + \frac{2\lambda^2 - \lambda pT + 2\pi^2}{\pi pT}\sin\frac{2\pi}{T}\tau. \tag{21}$$

Equations (20) and (21) serve to express the galvanometer throw θ_0 in terms of the charge Q, the characteristic discharge constant p, and the constant of the galvanometer for the case where the charge passes quickly. A similar expression for the case of an actual passage of a charge through the same circuit in a negligibly short time may be obtained from (20) and (21) by assuming p to be infinite. Representing these quantities by similar symbols primed, we have

$$(22) \qquad \theta_0' = \frac{GQ'T}{2\pi K} e^{-2\lambda(\tau'/T)} \sin 2\pi \frac{\tau'}{T}$$

and

$$(23) \qquad \tau' = \frac{T}{2\pi} \tan^{-1} \frac{\pi}{\lambda}.$$

The correction factor ϕ', the quantity by which the galvanometer throws must be multiplied in the case of the prolonged discharge to obtain the corresponding desired throws for the case of the impulsive discharge through the same circuit is evidently

$$(24) \qquad \phi' = \left[\frac{\theta_0'}{\theta_0}\right]_{Q'=Q} = \frac{e^{-2\lambda(\tau'/T)}}{e^{-2\lambda(\tau/T)}} \times \frac{\sin 2\pi\left(\frac{\tau'}{T}\right)}{\sin 2\pi\left(\frac{\tau}{T}\right)},$$

where τ and τ' are determined by (21) and (23). The determination of τ from (21) is not the formidable task that it appears at first sight. The assumption of different values for τ and the consequent evaluation of the left-hand term of (21) seems to be the easy method of operation. After the experience of one or two such determinations it will usually not be necessary to make more than two assumptions as to τ in order to evaulate it to the degree of accuracy warranted by the determinations of T and λ. Often the first approximation obtained by neglecting the left-hand member of (21) will suffice.

In the paper referred to by Peirce, a simple expression of the type (24) was not obtained. Nor does there seem, in following out his method, to be any simple means of arriving at any expression similar to (21) which may be used in determining τ.

In Fig. 1, there are represented for a particular case (No. 1, Table III.), as a function of the time, the relative positions of a galvanometer coil due to (*A*) an impulsive discharge and (*B*) an equal prolonged discharge. While various changes in the constants p, λ and T will shift these curves with respect to one another, their general shapes are characteristic for all discharges obeying (6). It is evident that $\tau > \tau'$ and that $\phi' > 1$.

In case one desires to compare the quantity of electricity which is discharged according to some particular decay law, with that discharged through the secondary coil of a mutual-inductance connected permanently in series with the galvanometer coil, (24) will suffice. However, if the comparison is to be made with the quantity discharged from a condenser, a somewhat different correction factor will be required. The latter discharge, assumed brief, represents an open circuit discharge for which B_1 in the previous development is to be replaced by B. Representing the

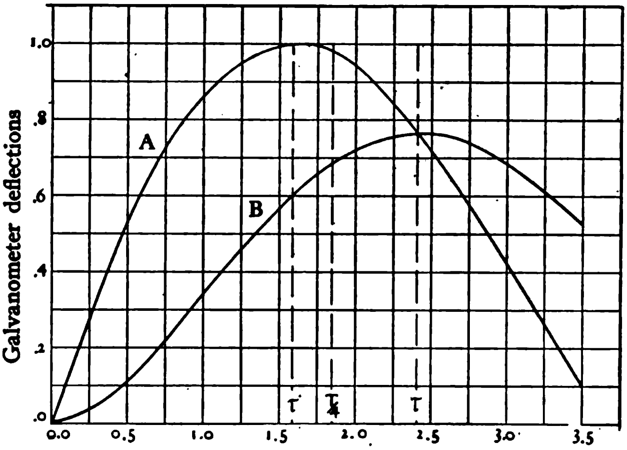

Fig. 1.

The deflections of a galvanometer on closed circuit as a function of time (A) for an impulsive discharge and (B) for a prolonged discharge of an equal quantity due to an intrinsic E. M. F. of the type $E = E_0e^{-pt}$.

quantities entering here by double primed (″) symbols, we have as an equation analogous to (24)

$$(25)\qquad \phi'' = \left[\frac{\theta_0''}{\theta_0}\right]_{Q''=Q} = \frac{T''}{T}\,\frac{e^{-2\lambda''\frac{\tau''}{T''}}\cdot\sin 2\pi\frac{\tau''}{T''}}{e^{-2\lambda\frac{\tau}{T}}\cdot\sin 2\pi\frac{\tau}{T}},$$

where τ is given by (21) and τ'' by

$$(26)\qquad \tau'' = \frac{T''}{2\pi}\tan^{-1}\frac{\pi}{\lambda''}.$$

T and T'' are related by a well-known expression derived from a comparison of $(B_1^2 - 4KD)$ with $(B^2 - 4KD)$, thus

$$(27)\qquad \frac{T''}{T} = \left(\frac{1+\frac{\lambda''^2}{\pi^2}}{1+\frac{\lambda^2}{\pi^2}}\right)^{1/2}.$$

This expression may be of considerable value in cases where it is difficult to obtain accurate determinations of T due to the periodic motion being heavily damped.

Condition II. $(B_1^2 - 4KD) > 0$.

Here represent β_1 and β_2 by

$$(28)\qquad \beta_1 = \gamma + \omega$$

and

$$\beta_2 = \gamma - \omega. \tag{29}$$

There results the expression analogous to (24),

$$\phi' = \left[\frac{\theta_0'}{\theta_0}\right]_{Q'=Q} = e^{-\gamma(\tau'-\tau)}\frac{\sinh\omega\tau'}{\sinh\omega\tau}, \tag{30}$$

where

$$e^{-(p-\gamma)\tau} = \cosh\omega\tau + \frac{\gamma^2 - \gamma p - \omega^2}{\omega p}\sinh\omega\tau \tag{31}$$

and

$$\tau' = \frac{1}{\omega}\tanh^{-1}\frac{\omega}{\gamma}. \tag{32}$$

Condition III. $(\beta_1^2 - 4KD) = 0$.

As a limiting case of condition II., there results

$$\phi' = \left[\frac{\theta_0'}{\theta_0}\right]_{Q'=Q} = e^{-\gamma(\tau'-\tau)}\frac{\tau'}{\tau}, \tag{33}$$

where

$$e^{-(p-\gamma)\tau} = 1 + \frac{\gamma^2 - \gamma p}{p}\tau \tag{34}$$

and

$$\tau' = \frac{1}{\gamma}. \tag{35}$$

PRELIMINARY GALVANOMETER TESTS.

Previous to considering the applicability of (24) and of (25) it is necessary (*a*) to consider the effects of neglecting the self-inductance in the galvanometer circuit, (*b*) to see if the fundamental assumption of a condition such that the torque due to a given current was independent of the galvanometer deflection throughout the range of deflections used was applicable, and (*c*) to see if there existed the peculiar condition of an apparent galvanometer resistance different from the true resistance as described by Peirce.[1]

As stated above, when there is a self-inductance in the galvanometer circuit, the equation of motion (5) can be solved. For the case of damped vibrations the equations are similar to those already given by (9) to (24), differing only from them owing to the introduction of another exponential term in the right-hand member of (9). For such an assumed case in which $\lambda = pT = \pi$, $r = 1{,}000$ ohms, and $L = 1$ henry, a case much worse than would be probable in practice particularly from the standpoint of the ratio r/L, the error due to neglecting the self-inductance was found to be only 0.2 per cent. This conclusion as to the magnitude of the error was verified by measurements made with the secondary of a 0.3 kw. transformer in series with the galvanometer. No effect due to its self-inductance could be detected with certainty. These facts were taken as justifying the assumption made in passing from (5) to (7).

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[1] Proc. Amer. Acad. of Arts and Sciences, 44, p. 63, 1908 (particularly pp. 79 and 80).

The fundamental assumption of a torque due to a given current, which is independent of the coil position throughout the range of deflections used, in other words the assumption that G is constant was tested by making determinations of λ at various times as the oscillations of the coil on closed and on open circuits died down. The constancy of G leads to the constancy of λ. Conversely constancy of λ, as may be shown, indicates the constancy of G. A somewhat more striking test however appears in connection with the third preliminary test.

This third test results from the indicated significance of the term B_1, in (8) thus

$$B_1 = B + G^2/r, \tag{36}$$

or

$$r = \frac{G^2}{B_1 - B} = \frac{G^2}{2K} \times \frac{2K}{B_1 - B}. \tag{37}$$

$2K/(B_1 - B)$ may be evaluated with the aid of (10), (11), (18) and (19). By platting $2K/(B_1 - B)$ as a function of r, Peirce, as noted above, found a relation of such a character as to indicate an apparent resistance for his galvanometer which was double the real resistance. The same test yielded for the galvanometer used by the writer results which are incorporated in Table II. Three conditions distinguished by different

TABLE II.

Data and Results for Third Preliminary Galvanometer Test.

Condition I.			Condition II.			Condition III.		
r Ohms.	λ	$\frac{2K}{B_1-B}$	r Ohms.	λ	$\frac{2K}{B_1-B}$	r Ohms.	λ	$\frac{2K}{B_1-B}$
∞	0.013	∞	∞	0.019	∞	∞	0.0139	∞
20,510	.148	15.50	1,310	.509	16.25	3,010	.1275	135.0
10,510	.282	7.81	1,110	.603	13.70	2,010	.1842	90.2
5,510	.529	4.108	910	0.735	11.29	1,310	.2756	58.8
3,010	0.988	2.250	710	1.013	8.30	910	.3935	40.7
2,510	1.216	1.860	610	1.112	7.63	710	.5040	31.7
1,510	2.330	1.125	510	1.370	6.34	510	.7000	22.9
$T_{r=\infty}$ = 4.18 sec.			$T_{r=\infty}$ = 15.7 sec.			$T_{r=\infty}$ = 30.6 sec.		

The galvanometer resistance of 510 ohms differs from that given in Table III due to a short circuiting of some of the turns of wire in the coil.

moments of inertia of the syspended system were made use of. Plats of these indicate that G is a constant and that the apparent resistance of the galvanometer, contrary to what was found by Peirce, is the same as the true resistance.

As another preliminary test, the accuracy with which (6) was satisfied experimentally was examined. Due to self-inductance in electric circuits a rigid fulfillment of (6) is not to be expected. In the arrangement of apparatus (Fig. 2) used in the experimental verification of (24), the self-inductance of the heating circuit leads to an expression of the type

$$E = E_0(e^{-pt} - e^{-p_1t}) \tag{38}$$

for the intrinsic E.M.F. instead of (6). Measurements with a known self-inductance introduced in various places showed that the time-constant $1/p_1$ must be negligible in comparison with $1/p$. Hence, experimentally (6) was shown to be applicable.

Experimental Verification of (24).

The galvanometer used was a type H instrument made by the Leeds and Northrup Co. The deflections were indicated by the movements of the image of a short, straight, thin tungsten filament on a screen from 4 to 7 meters distant from the galvanometer mirror. Due to the deflections of the galvanometer being alternately in opposite directions, it was impossible to take the precautions noted by Zeleny[1] against changes of set in the suspension. It was often noted, however, that this effect was small, certainly not as great as the deviations in the observed throws.

The method used in testing (24) is based on a slight modification of Corbino's method[2] of measuring the thermal capacity of a small, electrically conducting filament at high temperatures in an evacuated chamber. The writer's arrangement which will be discussed more fully in a forthcoming paper on the thermal capacities of tungsten and carbon, is indicated in Fig. 2. In order to eliminate the disturbance arising from the cooled portions of the filament $R + R'$ in one branch of the bridge as in Corbino's method, another filament R' of the same diameter but of shorter length than the filament $R + R'$ is introduced in the other branch in series with it. The two branches xx are made equal to one another. In effect for the purposes at hand, we have then in the bridge a single lamp filament R of uniform temperature throughout. Corbino has shown that, if the bridge has been balanced for steady currents first when the key k is closed and then secondly, by shifting only the contact c, when the key k is opened, there is a varying potential difference between the terminals of the galvanometer branch immediately following the opening or closing of k, which is of the exponentially decaying type. In his work, he concluded that the discharges were so nearly impulsive as to justify that assumption. This is not the case, however, with filaments of comparatively large cross-sections such as the writer has used. In some instances which have occurred the time-constants of the decaying discharges have been greater than the periods of the galvanometer. Data obtained even under such conditions were found to be very consistent when corrected according to (24) or to (25). Unfortunately where this condition prevails, an accurate determination of p by Corbino's method

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[1] Phys. Rev., 23, p. 399, 1906.

[2] Phys. Zeit., 13, p. 375, 1912.

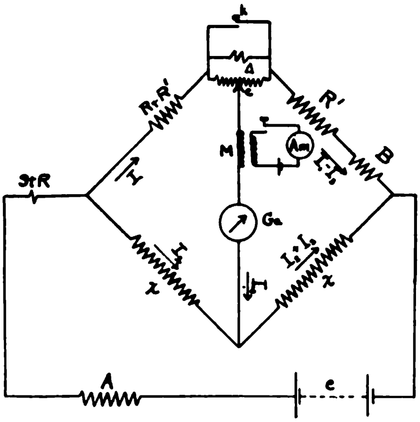

Fig. 2.
Arrangement of apparatus for testing (24).

TABLE III.

Test of (24) for a Discharge Through a Galvanometer Due to an Intrinsic E.M.F. of the Type $E = E_0e^{-pt}$ Where the Time-Constant $1/p$ (Fig. 2) is Equal to 1.06 sec.

r Ohms.	T Sec.	λ	θ_0' Div.	$\frac{\theta_0}{Q}$ $\frac{\text{Div.}}{\text{Microcoulomb}}$	$\frac{Q'}{\phi'}$ Microcoulombs.	ϕ'	Q' Microcoulombs.	$Q'r$ Microvolts × Sec.	$e^{-p\tau}$
10,540	7.35	0.692	9.07	20.08	0.452	1.296	0.586	6,180	0.103
5,280[1]	8.70	2.138	5.54	6.28	0.882	1.322	1.167	6,160	.115
15,540	4.30	1.355	7.29	32.45	0.225	1.680	0.378	5,870	.249
5,540	21.5	0.166	5.04	4.75	1.060	1.048	1.112	6,160	.0026
5,280[1]	21.5	0.354	2.17	1.955	1.110	1.047	1.162	6,140	.0033
5,540	15.3	0.234	6.56	6.38	1.030	1.088	1.120	6,210	.0125
5,280[1]	15.4	0.491	2.77	2.580	1.074	1.091	1.172	6,190	.0145
5,540	11.6	0.360	9.54	9.77	0.976	1.145	1.118	6,200	.032
5,280[1]	11.8	0.812	3.72	3.69	1.009	1.150	1.160	6,120	.038

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[1] For these sets the galvanometer whose resistance was 480 ohms was shunted with a 400 ohm resistance.

is very difficult. Other conditions less extreme have been selected, therefore, for the test of the foregoing theory. Certain data and results for such a test arranged in the order in which the data were taken, are incorporated in Table III. The various sets indicated were obtained essentially by varying the moment of inertia of the moving coil or by shunting it with a known resistance. The former method was carried out by adjusting two lead cubes that could be fastened at various positions on an aluminum rod which itself was attached to the bottom of the coil. In applying the above theory to cases where the method of shunting was employed, the galvanometer and shunt combination may be treated as a new galvanometer. It will be seen by the application of (20) and (21) or of (22) and (23), that the ratios of the deflections as given for the galvanometer when shunted and when unshunted for otherwise like conditions, are very closely as expected. Throughout the test the two steady current temperatures of the lamps, excepting for negligibly small changes due to the variations in x, were maintained constant. Consequently on opening and closing the switch k, the same quantity of electricity was in all cases discharged through the galvanometer circuit. The time-constant of this discharge $1/p$ according to Corbino's method was found to be 1.06 sec. The agreement indicated in the column of the table headed $Q'r$ is very good if one excepts the third set. Here the large value of λ and the shortness of the period made the direct determination of T, which was used, difficult. Had a method employing (27) been used, judging from later data obtained in other instances, there would not have been even this single exception. The constancy of the values for $Q'r$ indicate the verification of (24). As interesting data, there have been included in the last column of the table the relative values of the intrinsic E.M.F. at the times τ of the corresponding maximum elongations, and thus incidentally also, for the case of a galvanometer coil held motionless, the fractional parts of the total quantities of electricity discharged which remain at the times τ.

With (24) once checked, checking (25) may consist merely in verifying well-known relations for the ratios of the throws produced by condenser discharges to those produced by discharges from the secondary of a mutual inductance in series with the galvanometer. The writer, however, has tested (25) directly and has found the expected agreement.

The Determination of the Time-constant for a Discharge Obeying (6).

With the occurrence of a time-constant of the order of the galvanometer period, as was noted in the preceding subdivision, difficulty was experienced in obtaining p by Corbino's method. In such a case, a slight extension of the theory already given will suffice for its determination. Q' may then be found in the manner already indicated.

For this purpose, it is necessary that data similar to that indicated above shall be taken with at least two galvanometers of quite different periods. Different values of p must then be assumed and the corresponding values of $Q'r$ determined. That value of p which leads to a common value for $Q'r$ is the value sought. In general the greater the difference between the two values of ϕ' or of ϕ'' for a set, the greater the accuracy with which p may be determined. In illustration of this method, the data given in Table III. may be used. The data obtained in connection with tests 1, 2, 4 and 5 for two assumed values of $1/p$ lead to the values of $Q'r$ indicated in Table IV.

TABLE IV.

The Determination of p (Supposed Unknown) from Data Given in Table III.

Test.	$\frac{1}{p}$ (Assumed), Sec.	$Q'r$ Microvolts × Sec.	Tests Combined.	$\frac{1}{p}$ (Computed), Sec.
1	1.06	6,180	1 and 4	1.068
	1.10	6,080	1 and 5	1.078
2	1.06	6,160	2 and 4	1.060
	1.10	6,100	2 and 5	1.080
4	1.06	6,160		Av... 1.072
	1.10	6,140		
5	1.06	6,140		
	1.10	6,110		

As has been justified by repeated computations for small intervals, the relation between $Q'r$ and $1/p$ has been assumed to be linear for the interval 1.06 sec. to 1.10 sec. The computed values of the last column may therefore be readily obtained by noting the points of crossing of the straight lines on a plat of $Q'r$ as a function of $1/p$. The average value of $1/p$ thus obtained is 1.072 sec. This agrees extremely well with 1.06 sec. which was obtained by Corbino's method. In Table V., there are given the necessary data, computations and results for a discharge for which no satisfactory value of p could be obtained with the equipment at hand using Corbino's method. A slightly different method as to details is here indicated. For the writer's purpose, as will be noted in a later paper, the accuracy of this determination of p was quite satisfactory.

In order to decide whether (6) is fulfilled or not, several sets of data with galvanometers of different periods will be necessary. If a single assumed value of p leads to a common value for $Q'R$, whatever the period

TABLE V.

Data and Computations for the Determination of p for a Case where Corbino's Method was Difficult of Application.

r Ohms.	λ''	λ	T Sec.	θ_0 Div.	$\frac{\theta_0''}{Q''}$ $\frac{\text{Div.}}{\text{Microcoulomb.}}$	ϕ''		$Q'r$ Microvolts × Sec.		
						$p = 0.18 \frac{1}{\text{Sec.}}$	$p = 0.17 \frac{1}{\text{Sec.}}$	$p = 0.18 \frac{1}{\text{Sec.}}$	$p = 0.17 \frac{1}{\text{Sec.}}$	$p = 0.172 \frac{1}{\text{Sec.}}$
3,060	0.014	0.137	32.4	7.46	8.38	1.445	1.481	3,930	4,030	4,010
3,060	.016	.194	22.8	9.09	12.21	1.727	1.770	3,920	4,020	4,000
3,060	.018	.468	8.83	11.02	29.5	3.44	3.59	3,930	4,110	4,070
5,560	.018	.265	8.78	6.52	29.5	3.14	3.28	3,860	4,030	4,000
5,560	.013	.540	4.37	7.22	63.8	6.12	6.48	3,850	4,080	4,030
									Av.	4,020

of the galvanometer, (6) is fulfilled and vice versa. Thus the columns headed $Q'r$ of Tables III. and V. verify Corbino's theoretical conclusion as to the occurrence in his method of an E.M.F. obeying (6).

SUMMARY.

1. Expressions simpler and more complete than previous ones have been developed for obtaining ϕ' and ϕ'', the ratios of the deflections due to impulse discharges through a galvanometer on closed and on open circuits respectively to that produced by a prolonged discharge of an equal quantity due to an intrinsic E.M.F. obeying the exponential decay law.

2. The effect of self-inductance in the galvanometer circuit on the throws under all ordinary conditions is negligible.

3. The apparent resistance of the writer's galvanometer when used ballistically has been found to agree exactly with its real resistance, contrary to what was found by Peirce.

4. The expressions developed for ϕ' and ϕ'' have been experimentally verified, using a slight modification of Corbino's method of measuring the thermal capacity of filaments at high temperatures.

5. A method has been devised and applied for determining the time-constant of a discharge known to be of the exponentially decaying type.

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March, 1915.

ELECTRIC DOUBLE REFRACTION IN LIQUIDS.

BY HAROLD E. McCOMB.

THE velocity of light, vibrating in different planes in di-electric media, subjected to electric strain, was first investigated by Kerr[1] in 1894. After experimenting upon a number of liquids he concluded that the velocity of the component vibration polarized perpendicular to the lines of force was changed.

Later, G. Aeckerlein,[2] following a method similar to that used by Kerr, investigated the above effect in nitro-benzol and nitro-toluol. He found that in the former the perpendicular component is accelerated and the parallel component retarded, the ratio being about 2 : 1.

In the present investigation an attempt has been made to measure accurately the effect on each component.

APPARATUS.

The apparatus consisted of a Michelson interferometer mounted on a cement block. In the paths *A* and *B* were placed tubes of the liquid to be investigated. The tubes were ground so that they were practically the same length (22 cm.) and the ends covered with interferometer plates of the same optical thickness. The electrodes (made of brass) were placed within the tubes and held apart by glass plates of definite thickness. By placing the faces of the electrodes in one tube parallel to the plane of the table and in the other tube perpendicular to this plane the effect on either component could be measured without rotating the nicol. Later it was found more convenient to rotate the nicol and adjust all electrodes perpendicular to the table. The nicol *N* was arranged so that it could be quickly and accurately rotated 90 degrees, first transmitting light vibrating parallel to the table and then perpendicular. It was thus a simple matter to study the effect on each component in succession in the same tube. A direct-vision spectroscope was placed at *S* and a telescope at *T*. The total reflecting prism *P* was used to direct the light to the telescope *T* when adjustments were being made with sodium bands. All of the optical part of the apparatus except the light sources, the spectroscope, and the telescope was enclosed in a glass case in order to eliminate sudden changes in temperature and air currents.

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[1] J. G. Kerr, Phil. Mag., 37, 1894, p. 380.

[2] G. Aeckerlein, Physikalische Zeitschrift, 7, No. 17, p. 594.

Electrical Apparatus.

The potentials were supplied from a storage battery (1,000 volts) in series with three 1,200-volt generators and were measured by a Weston voltmeter (*V*) with multipliers giving ranges (0–150), (0–300), etc., to (0–6000). The arrangement of the commutator (described later) is shown at *C*.

Experimental.

The apparatus was first carefully adjusted for sodium bands using the prism *P* and the telescope *T*. The prism was then removed and the Nernst light *L* gave a clear channeled spectrum in the spectroscope. The tubes were then interposed and brought directly in line with the beams of light *A* and *B*. This step was the most difficult in the whole operation and was almost impossible to carry out without the use of small diaphragms. After adjusting the tubes so that the two fields of view were superimposed the air path *A* was increased or decreased by moving the mirror M_2 until the bands appeared. By applying the electric strain it was found that the bands usually appeared more quickly than when the liquids were simply allowed to stand. By applying the potential a distinct shifting of the bands was apparent, the amount depending upon the potential used. An attempt was made to measure accurately

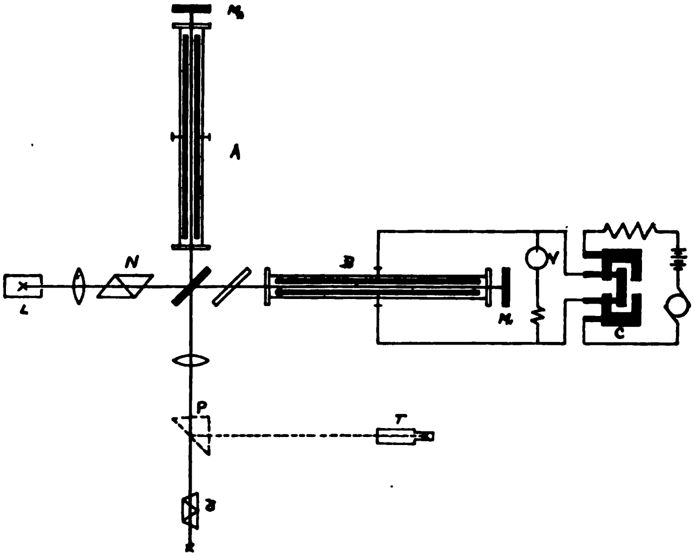

Fig. 1.

the shift produced by the application and quick removal of a definite potential. For this purpose the spectroscope was fitted with an eye-piece having movable and stationary cross-hairs. This method might have proved satisfactory had the field of view remained stationary but owing to the heating effect the whole field of view continually shifted. Nevertheless measurements were made until a potential was applied which gave a shift of *one band.* Up to this point the shift was quite large and measurable but for exactly *one band shift* the field of view apparently remained stationary. This might have been predicted because an instant shift of exactly one band could not be detected by the eye. A device was then made for rapidly and uniformly making and breaking the circuit. It consisted of a large commutator highly insulated which could be rotated at speeds varying from a few R.P.M. up to several hundred. It was found that a speed of about 200 R.P.M. was most satisfactory, there being one make and one break for each revolution. The field of view in the spectroscope was diaphragmed down so that different colors could be investigated. To obtain the retardation, then, for any wave-length it was only necessary to observe the potential required to produce a shift of one or more bands. Shifts up to three bands were thus measured with considerable accuracy. The results with nitro benzol are given in the tables which follow. In the first table the first column gives the wave-length; the second column, the potential difference (electrostatic) required to give an acceleration of one wave-length on the perpendicular component; the third column, the values of "$B_\perp$" (perpendicular component) computed from Kerr's law,

$$B = \frac{\delta a^2}{V^2 l},$$

in which δ is the retardation or acceleration, a the distance between the electrodes, l their length, and V the potential. The fourth column gives the potential difference required to give a retardation of one wave-length on the parallel component; the fifth column, the value of $B_\parallel$ (parallel component); and the last column the ratio $B_\perp$ to $B_\parallel$.

The second table gives the same for δ = two wave-lengths retardation and acceleration.

With nitro-benzol, *the component vibrating parallel to the lines of force is retarded amd the perpendicular component is accelerated, the ratio being 0.53.*

Several other liquids were investigated but none gave as satisfactory results as were obtained with nitro-benzol. In most cases the effects were too small to be measured accurately and distortions in the field of

Nitro Bensol.

(One Wave-length Retardation.)

March 20, 1914. Temperature 20° C.

Wave-length $\mu\mu$.	Potential Difference Electrostatic.	$B_\perp$	Potential Difference Electrostatic.	$B_\parallel$	Ratio $B_\perp/B_\parallel$
660	8.24	$87.\times10^{-7}$	5.96	$167.\times10^{-7}$	.52
620	7.88	95.	5.85	173.	.55
580	7.57	103.	5.39	204.	.51
540	7.15	116.	5.22	218.	.53
660	8.17	89.	5.95	167.	.53
				Mean......	.53

Nitro Bensol.

(Two Wave-lengths Retardation.)

Wave-length $\mu\mu$.	Potential Difference Electrostatic.	$B_\perp$	Potential Difference Electrostatic.	$B_\parallel$	Ratio $B_\perp/B_\parallel$
660	11.58	$88.\times10^{-7}$	8.46	$166.\times10^{-7}$	.53
620	11.21	94.	8.10	181.	.52
580	10.83	101.	7.81	194.	.52
540	10.17	115.	7.28	224.	.51
660	11.60	88.	8.48	165.	.53
				Mean......	.53

Note.—Length of electrodes, 20 cm. (effective path 40 cm.). Distance between electrodes, .154 cm.

view caused considerable trouble. Carbon bi-sulphide and chloroform could be easily investigated with longer tubes or higher potentials but the effect is too small on either to give one band shift with the apparatus described here. The following qualitative measurements were made:

With Carbon Bi-sulphide.—Potentials were supplied from a static machine and measured approximately by means of a spark gap. By allowing the condensers to charge and discharge rapidly the effect was similar to that obtained with the commutator. Using this method no effect was observed upon the component vibrating perpendicular to the lines of force up to a 4 mm. spark gap potential. The other component, that is, the component vibrating parallel to the lines of force, is retarded and apparently is the only component affected.

With Chloroform.—Both components are accelerated, the component vibrating parallel to the lines of force is the larger.

In conclusion the writer wishes to acknowledge his indebtedness to Dr. C. A. Skinner for help and inspiration received during this work.

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THE RELATION BETWEEN THE ALPHA-RAY ACTIVITIES AND RANGES OF RADIUM AND ITS SHORT-LIVED PRODUCTS.

By Herbert N. McCoy and Edwin D. Leman.

IN a recent paper[1] it has been shown that the ratio between the α-ray activity of radioactinium and that of its products is in good agreement with the value calculated from the equation $I = kR$, where I is the ionization current in air due to a single α-particle, R is the range of the α-particle, and k is a constant for α-particles of all ranges.[2] McCoy and Viol[3] had previously shown that the relative α-ray activities in the thorium series, as calculated from the same equation, are in good accord with the experimental values. In this paper we wish to show that the relative activities of radium and its short-lived products are also in good agreement with those calculated from the known ranges.

The latest available data on the radium series[4] which we shall use in this paper are given in Table I.

Table I.

The Radium Series.

	Symbols.	Period.	Rays.	Ranges, Cm. at 15° C.
Radium..........	Ra	1730 years	α, β	3.30
Emanation.......	Em	3.85 days	α	4.16
Radium *A*.......	Ra*A*	3.00 min.	α	4.75
Radium *B*.......	Ra*B*	26.7 "	β	
Radium C_1.......	RaC_1	19.5 "	α(?), β	
Radium C_2.......	RaC_2	1.4 "	β	
Radium C'.......	RaC'	10^{-6} sec. (?)	α	6.94

The accepted scheme of disintegration in this series, according to Fajans[5] is as follows:

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[1] McCoy and Leman, Phys. Rev., *4*, 409 (1914).

[2] Geiger, Proc. Royal Soc., A, *82*, 486 (1909); A, 83, 505 (1910). Taylor, Phil. Mag., *21*, 571 (1911); *26*, 402 (1913).

[3] McCoy, Phys. Rev., *1*, 393 (1913).

[4] Kolowrat, Le Radium, *11*, 1 (1914).

[5] Phys. Zeit., *13*, 699 (1912).

$$\begin{tikzcd}
& & & & & \mathrm{Ra}C_2 \arrow[r, "\beta"] & ? \\
\mathrm{Ra} \arrow[r, "{\alpha, \beta}"'] & \mathrm{Em} \arrow[r, "\alpha"'] & \mathrm{Ra}A \arrow[r, "\alpha"'] & \mathrm{Ra}B \arrow[r, "\beta"'] & \mathrm{Ra}C_1 \arrow[ur, "\alpha"] \arrow[r, "\beta"'] & \mathrm{Ra}C' \arrow[r, "\alpha"'] & \mathrm{Ra}D \arrow[r, "\beta"'] & \mathrm{Ra}E \arrow[r, "\beta"'] & \mathrm{Ra}F \arrow[r, "\alpha"'] & {}
\end{tikzcd}$$

According to this view, the product formerly called radium C is complex: C_1, which is the product of B, disintegrates in two ways; the first (principal) with the production of a β-particle giving C'; the second (subordinate) with the expulsion of an α-particle, giving C_2. The product C' also gives α-rays, and of every 10,000 α-particles produced by the C components, all but three are due to the change of C' into D, the balance being due to the change of C_1 into C_2.[1] If we assume that these conclusions are essentially correct, we see that the effect on the activity caused by a minute fraction of the α-particles of radium C having a different range from those of the main fraction, would be negligibly small. We shall, therefore, neglect the complexity of C in the discussions in this paper, merely pointing out that the present work furnishes no data regarding this important question.

The method of determining the relative α-ray activities of Ra and its short-lived products consisted in preparing a Ra-$BaSO_4$ film free from all of the subsequent products of Ra, and measuring its initial and final activities. The activities of such films increased for about six weeks after the preparation of the film and then remained practically constant during several months of observation, the constant activity in each case being taken as the final. The Ra-$BaSO_4$ film, free from its subsequent products, was prepared in the following manner: One c.c. of a solution of pure radium chloride in dilute hydrochloric acid was diluted to 10 c.c.; the solution was heated to its boiling point and a current of air bubbled through it for thirty minutes, the solution being kept near its boiling point and a few c.c. of water being added from time to time to replace that lost by evaporation. This procedure kept the solution free from emanation, and allowed RaA to decay practically completely. A few drops of lead acetate solution were then added and hydrogen sulphide passed in. The lead sulphide, which was precipitated, removed B, C, D, E, and F. The precipitate was rapidly filtered off, and a current of air again bubbled through the filtrate, for ten minutes, keeping it near its boiling point and the volume constant. Lead sulphide was again precipitated in the solution, the precipitate filtered off, and the filtrate again treated in the manner just described, making a total of three precipitations of lead sulphide, and removing practically every trace of the products of radium. The various operations to this point had taken about fifty minutes. The filtrate from the last treatment was put into a 15 c.c. centrifuge tube, one c.c. of $N/100$ barium chloride solution added, then a few drops of dilute sulphuric acid. The solution was well shaken, and then centrifuged. The supernatant solution was decanted from the precipitate, and the latter was well washed, by decantation, with water acidified with a few drops of HCl, and finally with alcohol. A small portion of this precipitate was spread as uniformly as possible, with the aid of a glass rod and a little alcohol, over a flat polished brass plate, about 7 cm. in diameter. When the alcohol had evaporated, the less firmly adhering particles were brushed off, care being taken to guard the edges and back of the plate from radioactive contamination. The films so prepared were so thin as to be almost invisible; the differential absorption of α rays in such films was therefore negligibly small.

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[1] Fajans, loc. cit.

The time of precipitation of the sulphate was taken as zero time, as at this moment the precipitate was free from all of the subsequent products of radium. That the above method completely freed the radium from all of its active products was shown both by control experiments[1] and by the fact that the activity increased at a regular rate from the start. About thirty minutes elapsed between the time when the sulphates were precipitated and the time of making the first measurements. The activity measurements were made in a gold-leaf electroscope as previously described,[2] the active films being placed 7 cm. below the charged electrode, thus allowing all rays to reach their full ranges. Sufficient potential (about 600 volts) was used to insure practically complete saturation currents for the weak ionization produced. All activities were measured in comparison with a standard film of uranium oxide, the activities given being in terms of this standard. All measurements were made with the greatest care, and corrections were made for the accurately determined natural leak, which in every case was less than one per cent. of the standard. The initial activity of each film was less than, the final activity greater than, the standard. The activity increased nearly linearly for the first six hours so that by a small extrapolation the activity at time zero could be determined with a high degree of accuracy. The activities in terms of the standard are given in Table II. for two films.

TABLE II.

The Initial and Final Activities of Radium (Uncorrected).

Film.	Initial Activity I_0.	Final Activity I.	Ratio Uncorrected.
1	0.858	4.325	5.043
2	0.558	2.832	5.075

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[1] Compare the work of McCoy and Viol, loc. cit., on the separation of Th-*B*-*C*-*D* from Th*X*.

[2] McCoy and Ashman, Am. Jour. Sci., *26*, 521 (1908).

But these results are subject to three corrections, viz.: the activity due to the β-rays, the escape of emanation from the film either by diffusion or by recoil, and the loss of other products by recoil.

The activity due to β-rays was determined by placing consecutive layers of aluminium foil over the Ra-$BaSO_4$ film, the first layer being of sufficient thickness to absorb all α-rays, and measuring the activity with each additional layer in the same electroscope as was used for the α-ray measurements. By plotting the activities against the thickness of the covering, and extrapolating to the axis of the activities, the β-ray activity could be ascertained with a fair degree of accuracy. This activity must be subtracted from the final activity of the film.

Since Kolowrat has shown that[1] the β-ray activity of radium free from its products is only 2 per cent. of the β-ray activity of radium in equilibrium with its short-lived products, and since the β-ray activity of the latter as measured in our electroscope was only about 0.5 per cent. of the α-ray activity, it follows that it is not necessary to apply any correction for β-ray activity of the radium itself.

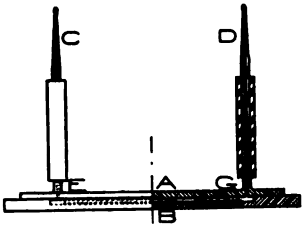

Fig. 1.

The amount of emanation lost by the film was determined by the use of a circular brass box as shown in Fig. 1. The cover, *A*, fitted with two small bore tubes *E* and *G*, was ground so as to fit very tightly over the lower compartment *B*. In the lower compartment was a recess about 0.2 cm. in depth and 8 cm. in diameter. Small bore glass tubes drawn out at one end, *C* and *D*, were attached to the tubes *E* and *G* by means of short pieces of thick-walled rubber tubing. The Ra-$BaSO_4$ film was placed in *B*, the cover *A* fitted on, and all joints sealed with wax. The ends of *C* and *D* were then sealed by fusion. After an interval of 40 days or more, the emanation which had accumulated was drawn into an emanation electroscope by a stream of air, care being taken to prevent any loss of the accumulated emanation and also to prevent any diminution of pressure within the box which might withdraw some of the Em from the film. The rate of discharge of the electroscope was measured, after the emanation had stood in it for three hours.

In order to find what fraction this quantity of Em was of the equilibrium quantity in the Ra-$BaSO_4$ film, two additional determinations were necessary. One c.c. of the original radium solution was diluted and then freed from subsequent active products as described in a preceding paragraph. By means of a small weight-pipette, an accurately weighed portion of this solution was taken and uniformly distributed over the surface of a flat platinum plate, and evaporated to dryness. The activity of the residue, which was entirely invisible, was measured within twenty minutes, and the measurements extended over a short interval in order to be able to get the initial activity by extrapolation. To find the activity of the emanation from this quantity of radium, a known portion of the solution in the weight-pipette was run into a small round-bottom flask containing about 10 c.c. of dilute hydrochloric acid. The flask was well stopped with a two-hole rubber stopper fitted with delivering tubes, one of which extended into the solution. A current of air was bubbled through the solution for 30 minutes to drive off the accumulated emanation, and the flask then sealed by fusing the ends of the delivery tubes. After an interval of a few days, the emanation was drawn into the emanation electroscope, by allowing air to bubble through the solution which was heated near its boiling point. After three hours, the rate of discharge of the electroscope was measured.

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[1] Le Radium, 7, 269 (1910).

The corrections for loss of emanation by the film were made as follows:

Initial activity of film No. 1	0.858
Initial activity of Ra on the platinum plate	.660

The radium on the platinum plate was obtained from 1.4942 gm. of solution. 1.5738 g. of the same solution gave after three days, 21.5 hours, a quantity of Em which discharged the electroscope in 46.45 seconds. Since for three days 21.5 hours, $1 - e^{-\lambda t} = 0.5036$, the equilibrium amount of Em from the solution would have discharged the electroscope in $0.5036 \times 46.45 = 23.40$ sec. Therefore the equilibrium amount of Em from 1.4942 gm. of this solution would discharge the electroscope in 24.64 sec. That is, a radium film, free from all subsequent products of radium, having an initial α-ray activity of 0.660 produces an equilibrium quantity of emanation which discharges the emanation electroscope in 24.64 sec. It then follows that the equilibrium quantity of emanation from film No. 1, which has an initial activity of 0.858 would discharge the emanation electroscope in 18.97 sec. The emanation which had escaped from film No. 1, when the latter had been sealed up 40 days or more, discharged the emanation electroscope in 1,748 seconds, therefore 1.08 per cent. of the equilibrium quantity of Em escaped from the film. This means that the quantity of emanation and the short-lived products in the film is 1.08 per cent. too low. In this film, the activity of the subsequent products of Ra is $4.297 - 0.858 = 3.439$, which value is 1.08 per cent. too low, hence the true activity of the products, if no Em had escaped, would be 3.476.

To find the loss of activity due to recoil, a polished brass plate 7 cm.

in diameter was placed 1 mm. above and completely insulated from film No. 1. A potential of 110 volts was maintained for six weeks, the upper plate being kept negatively charged. The activity of the plate was measured as quickly as possible after removing the potential, four minutes elapsing from the time the potential was removed to the mean time of making the measurements. The activity of the active matter which collected on the plate was 0.0374. Assuming that the active matter on the plate at the instant the potential was removed was Ra*A*, Ra*B*, and Ra*C* in equilibrium, the activity of the matter on this plate four minutes after the potential is removed is approximately 70 per cent. of its initial value.[1] Therefore the initial activity of the matter on the plate was 0.0534. To find what quantity of the matter on the plate is due to active deposit from escaped emanation and what quantity is due to direct recoil, it is necessary to recall that the emanation lost by this film was 1.08 per cent. of the equilibrium quantity, or the activity of the products, Em, Ra*A* and Ra*C*, lost was 0.037. Assuming that the activities are proportional to the 2/3 powers of the ranges, the fraction of the activity due to Ra*A* + Ra*C* is 65 per cent. of the total activity due to Em + Ra*A* + Ra*C*, or 0.0241 and that due to recoil is .0534 − .0241 = .0293.[2]

Table III. gives the results of two determinations. The final activity is corrected for β-ray activity, loss of emanation, and loss by recoil, these corrections being determined separately for each film:

Table III.

The Initial and Final Activities of Ra (Corrected).

Film.	Initial Activity I_0.	Final Activity I.	$\frac{I_0}{I}$.
1	0.858	4.363	5.085
2	0.558	2.863	5.133
			Mean . . 5.109

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[1] Rutherford, Radioactive Substances and their Radiations (1913), page 491.

[2] It must be pointed out that this value is calculated on the assumption that at the instant the potential is removed, the active matter on the plate is Ra*A* + Ra*B* + Ra*C* in equilibrium, and there is a decided drop in activity before the first measurement is made, due to the rapid decay of Ra*A*. In the case of the active matter due to active deposit we do have this equilibrium, but in the case of recoil atoms, there is in all probability an excess of Ra*C* atoms, over the equilibrium number of Ra*A* atoms. This would mean that the percentage of the activity which decayed during the interval between the time the potential was removed and the time of measurement would not be so great as that calculated upon complete equilibrium, and the value of the loss by recoil would be even less than that calculated above. However, the loss by recoil is so small, that the value calculated above is certainly correct within experimental error, and it represents the maximum value.

In the series Ra-Em-Ra*A*-Ra*C* it is very probable that each member when present in equilibrium amount produces the same number of α-particles per unit time, if this is so, the equation

$$I = kR^{2/3}$$

leads to the theoretical results shown in Table IV.

TABLE IV.

	Ranges at 15°.	$R^{2/3}$.	Relative Activities.	
			Calculated.	Found.
Ra	3.30	2.217	1.00	[1.00]
Em	4.16	2.586	1.17	
Ra*A*	4.75	2.826	1.28 } 4.09	4.11
Ra*C*	6.94	3.639	1.64	

The only previous determination of the relative activities of radium and its products was made by Boltwood.[1] In these experiments the films were made by the evaporation of a chloride solution. Since such films gave off very large fractions of the emanation produced (in one case as high as 65 per cent.) it is not surprising that the results obtained were not very accurate. Instead of a ratio of 4.11 as found by us (last column, Table IV.) Boltwood found 4.65. For several years this result was looked upon as satisfactory,[2] since it was in good agreement with that calculated upon the assumption that the number of ions produced by an α-particle is proportional to the first power of its range[3] instead of the two-thirds power.

TABLE V.

Relative Alpha-Ray Activities.

Ratios Measured.	Found.	Calculated.
Thorium *X* and products to radiothorium[1]	3.66	3.60
Thorium C_1 and C_2 to radiothorium[1]	1.54	1.56
Actinium *X* and products to radioactinium[2]	4.67	4.63
Radium emanation and products to radium [3]	4.11	4.09

[1] McCoy and Viol, loc. cit.

[2] McCoy and Leman, loc. cit.

[3] McCoy and Leman, this paper.

The good agreement of our results with the theoretical value as calculated by the equation $I = kR^{2/3}$, the correctness of which may be considered as already established, shows that only those members which we have considered play significant parts in the α-ray activity of the radium series, and that the accepted ranges are at least approximately correct.

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[1] Phys. Zeit., 7, 489 (1906); Le Rad., 3, 170 (1906).

[2] Rutherford, Radioactive Substances, p. 447 (1913).

[3] Boltwood, loc. cit.

In Table V the results of the recent investigations carried out in this laboratory along analogous lines are brought together.

The values headed "Found" are the relative observed α-ray activities of the indicated substances. The calculated values were obtained by means of the equation $I = kR^{\frac{2}{3}}$, according to which the number of ions produced by an α-particle is proportional to the 2/3 power of its range.

Kent Chemical Laboratory,
University of Chicago,
March 3, 1915.

THE FLUORESCENCE OF SOME FROZEN SOLUTIONS OF THE URANYL SALTS.

BY H. L. HOWES.

IN the recent work done by Nichols and Merritt[1] on frozen solutions of the uranyl salts at liquid air temperature it was noticed that there were various changes in the spectra of those solutions at temperatures intermediate between + 20° C. and − 185° C. The object of this investigation was to study these spectra at the intermediate temperatures. It was known that in general the spectra consisted of rather broad bands with well marked crests, and that the frequency interval between the bands was constant.

EXPERIMENTAL METHOD.

For the study of the spectra, except where otherwise specified, a Hilger constant deviation spectrometer was used.

The apparatus for the cooling and excitation of the substances under observation was designed to enable the observer to hold the temperature of the specimen constant at any temperature between 0° and − 180° C. The mounting consisted of a cylindrical copper block *M* (Fig. 1), the top of which was bored to receive a small test-tube *F*, which contained the fluorescent solution. The side of the block was channelled to let the exciting light fall on the specimen; and to let the fluorescent light out. To the bottom of this copper block was soldered a cylinder of sheet copper, which could be partially or completely covered by the liquid air in the unsilvered Dewar bulb *D*, thus producing different temperatures in the specimen. This mounting was rigidly suspended from above by partially non-conducting material. The Dewar bulb was fastened to an adjustable support *H*, and the mounting could be submerged in the liquid air to various depths by raising or lowering the bulb by means of cord *R*.

Fluorescence was excited by the rays from a carbon arc *A*. The light passed successively through a water cell *W*; a large short-focused condenser *C*; and a solution of ammonio-copper sulphate *B*. This solution absorbed all of the exciting light of a wave-length greater than .4780 μ, so that the fluorescent light, which entered the collimator slit *S* of the spectrometer, could be viewed on a black background.

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[1] PHYS. REV., Vol. III., June, 1914.

A small resistance coil *T* was inserted in a glass tube, which was always placed in the middle of the solution. The temperatures were recorded on a Callendar recorder. The massive copper block *M* served to reduce the vertical temperature gradient in the frozen solution to less than 1° per centimeter. It made the apparatus rather slow in responding to changes, but afforded an excellent control of temperature.

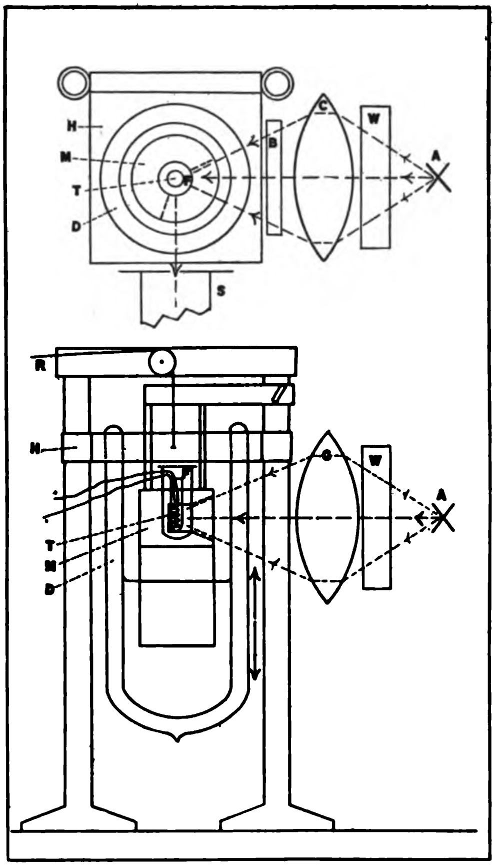

Fig. 1.

The salts were carefully weighed and "normal" solutions were prepared.[1] Acid solutions were made by adding a definite volume of the commercial concentrated acid to a definite volume of a water solution of known concentration.

Although readings were taken and tables made in Ångström units of wave-length the diagrams of spectra were plotted on an arbitrary scale of frequencies; *i. e.*, 1/A. u. × 10^4. Both scales were placed under each plot for the convenience of the reader.

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[1] The term "normal" solution, as used in this paper, means one which contains the same number of grams of solute to the liter of solvent as the number which represents the molecular weight of the particular salt dissolved.

PRELIMINARY STATEMENT OF THE RESULTS.

In general, when a solution of a uranyl salt was cooled slowly to liquid air temperature its spectrum changed in two or more ways. The spectrum always appeared brighter at lower temperatures than at room temperature. There was always a shift of the spectrum, either toward the red or toward the violet, due to the change in temperature.

Generally, too, the bands were narrower at lower temperatures.

The more dilute the solutions the dimmer were the spectra.

In the uranyl nitrate solutions the rate at which the solution was cooled determined what spectrum would be produced, as regarded the number and position of the bands.

The effect of diluting the water solutions with small proportions of acid was to produce a shift in the positions of the bands, and in larger proportions, to entirely change the character and appearance of the spectrum.

URANYL SULPHATE IN WATER.

Uranyl sulphate presented spectra consisting of broad bands. At + 20° the spectrum of the normal solution consisted of four dim bands, which were equally spaced when plotted on a scale of frequencies. The bands shifted toward the violet as the temperature was lowered. This shift attained a maximum when the temperature was approximately − 100°. (See Table I.) On further fall in temperature the bands shifted toward the red. As a result of this reverse shift the bands occupied nearly the same positions at − 180° as they formerly had at a temperature of − 60°.

The one-tenth normal solution of the uranyl sulphate gave a series of bands which occupied nearly the same positions as those of the normal solution. These bands attained their maximum shift toward the violet at − 90° and then shifted towards the red. To ascertain the effect of the rate of cooling a test-tube containing this solution was suddenly plunged into liquid air and excited to fluorescence. The bands were similar to those of the same solution which had been slowly cooled. If there were any change in position it was within the experimental error of observation.

The .01 normal solution showed the shift toward the violet and the reverse shift. The temperature at which maximum shift occurred was − 100°.

The .001 normal solution gave vague broad bands at all temperatures. All of the bands were found to be nearer the violet than those of the stronger solutions. The maximum shift toward the violet was found to occur when the temperature was − 120°.

Table I.

Uranyl Sulphate in Water; Normal Solution.

Temperature.	Band *b*.	Band *c*.	Band *d*.	Band *e*.	Band *f*.	Band *g*.
+ 20°	....	....	5,641	5,383	5,143	4,927
0	....	....	5,641	5,383	5,141	4,926
− 35°	....	5,934	5,641	5,378	5,141	4,927
− 60°	6,229	5,928	5,637	5,376	5,137	4,924
− 90°	6,227	5,923	5,635	5,370	5,131	4,919
−120°	6,230	5.923	5,634	5,370	5,133	4,919
−150°	6,235	5,924	5,634	5,373	5,136	4,921
−180°	6,241	5,924	5,636	5,375	5,140	4,926

Jones and Strong,[1] in their study of the absorption spectra of the uranyl salts, noticed that the absorption band at 4,910 A. u. shifted 15 A. u. toward the red when the temperature was raised from + 5° to + 84°. This is in agreement with the movement of fluorescence band *g* (Table I.) normal solution which shifted 8 A.u. toward the red when the temperature was raised from − 90° to + 20°. The shift is the same in direction in both the fluorescence and absorption spectra of the normal solution for temperatures above − 100° C.

Uranyl Sulphate in Sulphuric Acid.

The one-tenth normal aqueous solution was added to the sulphuric acid, the first solution containing 40 c.c. of the solution to 1 c.c. of the acid. The spectrum was shifted towards the violet at − 90°. When the cooling process was carried to − 180° the bands shifted back toward the red.

The bands occupied approximately the same position as did the bands of the 1/10 normal aqueous solution at the corresponding temperatures. Band *g* was the exception, as it was shifted, at all temperatures, nearer to the red. This decreased the frequency interval between bands *f* and *g* at all temperatures.

Another acid solution was made by mixing equal volumes of the 1/10 normal solution and of the acid. The spectrum of this solution, at + 20°, was nearer the red than that of the aqueous solution at + 20°.

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[1] Carnegie Inst. of Washington, No. 130, p. 109.

Jones and Strong[1] also found that the absorption spectrum of the uranyl sulphate was shifted toward the red by the addition of sulphuric acid to the aqueous solution. The effect of slowly cooling this solution to − 185° was to produce a marked shift toward the violet. Band *g* shifted 72 A.u. between + 20° C. and − 180° C. This shift toward the violet even continued through the range from − 90° to − 180°. The bands were equally spaced in frequency units.

URANYL POTASSIUM SULPHATE IN WATER.

The spectra of the aqueous solutions of this salt resembled those of the single sulphate in appearance. The bands were broad, and, in the stronger solutions, very brilliant.

The 1/15 normal solution was almost saturated at + 20° C. When the temperature was lowered the spectrum showed a slight increase in the frequency interval, and a pronounced shift when − 150° was reached. Between − 120° and − 150° the shift toward the red which began at 0°, increased rapidly, and continued to the lowest temperature. At all temperatures between − 30° and − 185° the space between the bands was approximately 86 units, on the scale of frequencies.

The 1/150 normal solution gave spectra which at first shifted slightly toward the violet and then shifted toward the red. The frequency interval was again 86 units.

To ascertain the effect of sudden cooling on the bands of this solution the solution was suddenly plunged into liquid air. The spectrum at − 180° was the same as that of the slowly cooled solution as regarded position and appearance of the bands.

The 1/1500 normal solution gave vague spectra. The bands appeared to be almost smothered by the continuous fluorescent spectrum which formed the background. Another trial with the same solution gave a spectrum which showed no decided tendency to shift toward the red.

The 1/15,000 normal solution gave a spectrum which consisted of dim, hazy bands. The effect of dilution was to produce an enormous shift of all of the bands toward the violet; and to further decrease the interval between bands. The effect of lowering the temperature was to shift the bands toward the violet until − 120° was reached; while on further cooling a reverse shift toward the red occurred.

The 1/150,000 normal solution gave, at − 185°, a spectrum which consisted of three very dim bands. The middle band, at 5239 A. u. corresponded in position to the band at 5235 A. u. of the 1/15,000 normal solution, but the interval between the bands was smaller.

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[1] Loc. cit., p. 135.

The effect of ***dilution*** on the frequency interval was to decrease it. Both the 1/15 and 1/150 normal solutions had bands which were spaced 86 + frequency units apart; the 1/1,500 bands were 82 units apart; the 1/15,000 bands were 80 units apart, and the 1/150,000 bands 77 frequency units apart.

URANYL POTASSIUM SULPHATE IN SULPHURIC ACID.

Fig. 2 shows the bands of an acid solution made by adding 5 c.c. of the 4/15 normal solution to 1 c.c. of sulphuric acid. The spectra shifted toward the violet when the solution was cooled, and attained their maximum shift at − 120°. Further cooling to − 180° caused the bands to shift back toward the red. In the manner of shifting, the spectra of this solution resembled closely those of the stronger solutions of uranyl sulphate in water. The frequency interval became shorter as the temperature was lowered, but appeared to be constant at any one temperature.

Another sulphuric acid solution was made by adding 1 c.c. of the 4/15 normal solution to 1 c.c. of the sulphuric acid, which showed a constant tendency to shift toward the violet as the temperature was lowered from + 20° to − 180°. The total shift amounted to about 40 A. u. Here, too, the interval between the bands decreased as the temperature of the solution was lowered.

The last solution studied was the most interesting. It was made by adding one part of the solution to fifty parts of sulphuric acid. It was observed that the shift was quite irregular until a temperature of − 150° was reached, when the bands nearer the violet doubled. At − 180° there was a greater tendency toward resolution. The component bands were evenly spaced on the frequency scale, and formed separate series.

URANYL CHLORIDE IN WATER.

The spectra of the uranyl chloride in solution consisted of single bands, which were about 75 A. u. in width and were separated by a black background. In the latter respect they differed from the spectra of the sulphates, as the background for the bands of the sulphates was always filled with a very dim continuous fluorescence. The crystalline chloride was very deliquescent and very soluble in water, but the spectra were not nearly so brilliant as those of the sulphates.

The bands of the saturated solution were first measured at − 90°, and were found, except for the two end bands, to be evenly spaced in frequency units. When the temperature was gradually lowered to − 180° the bands appeared brighter, and shifted slightly towards the red, so that band 5154 A. u. shifted only six A. u. as the temperature was reduced to — 180°.

The effect of adding more water to make a 3.0 normal solution was to shift the spectrum as a whole about 15 A. u. toward the violet, without changing the actual distances between the bands. The effect on the positions of bands of changing the temperature was small. The shift was slightly toward the red for all bands except the violet band, which was fixed. This band, as well as the red band, was again closer to its neighboring band than the constant interval of the series.

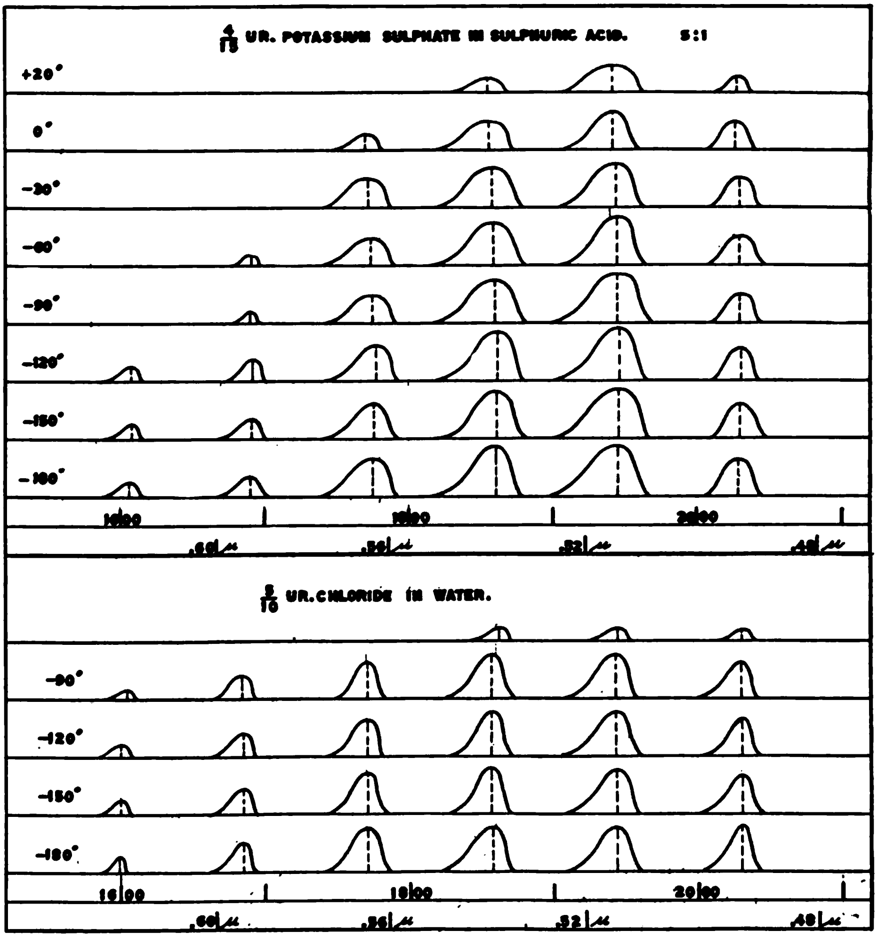

Fig. 2.

The 1.5 normal solution was still more stable, since the bands, except for the red, are not moved by changing the temperature. The .5 and .05 normal solutions were also practically unaffected by changes of temperature. See Fig. 2.

Extreme dilution with water would possibly have produced a shift in the spectrum as a whole, but so far as these results go, it would seem that the aqueous solutions of the uranyl chloride are the most stable of any of the uranyl salts in solution.

Uranyl Nitrate in Water.

The first results obtained by changing the temperature of various solutions of the uranyl nitrate were often contradictory. These results were only made to accord when the same slow method of cooling the solution was employed. Nichols and Merritt[1] found that the spectrum of uranyl nitrate consisted of alternate broad and narrow bands. An entirely different spectrum was obtained from the same salt by a slower method of cooling to liquid air temperature. Five different spectra were photographed from the same solution at − 180°. (See Fig. 3.) These five spectra show the different degrees of resolution obtainable

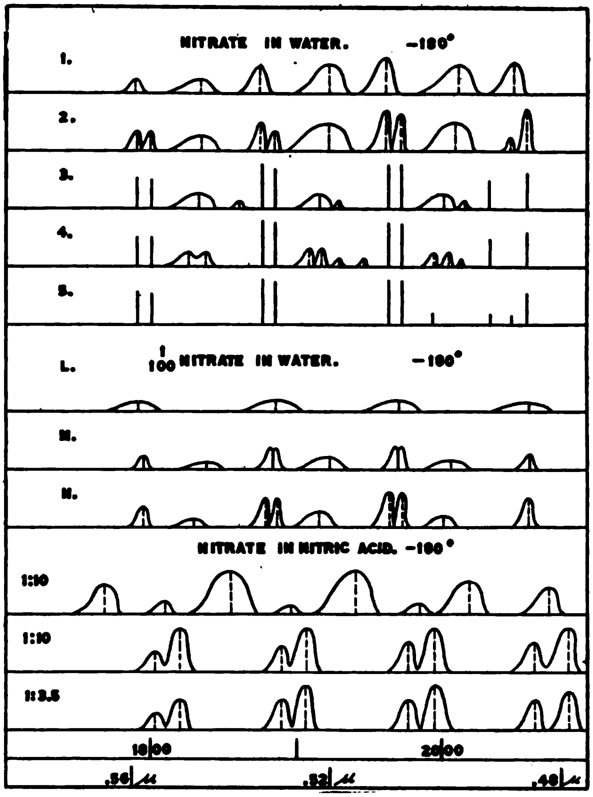

Fig. 3.

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[1] Loc. cit., p. 459.

by varying the rate of cooling. No. 1 was obtained by suddenly plunging a test-tube of the normal solution into liquid air: numbers 2, 3 and 4 show the varying degree of resolution obtained by slower cooling. No. 5 required about ten minutes to cool from + 20° to − 180° C. The double bands of this spectrum are in the same position as those of the crystallized nitrate at − 180° and all well resolved.

The spectra of the 1/100 normal solution were similarly affected (see Fig. 3) by retarding the rate of cooling. Spectra *L*, *M* and *N* are the results of successively slower rates of cooling.

Uranyl ammonium nitrate and uranyl potassium nitrate gave almost as good resolution as the uranyl nitrate.

THE EFFECT OF TEMPERATURE ON A SLOWLY COOLED NORMAL SOLUTION OF URANYL NITRATE.

Since the changes in the spectrum of the normal solution are very striking and also typical of several other more dilute solutions a detailed study of them was made. (See Fig. 4.) At + 20° only two dim bands were seen, one at 5,323 A. u. and the other 5,088 A. u. At 0° a slight increase in intensity was noted, so that four bands could be measured, and at − 25° several phenomena occurred simultaneously. The Callendar recorder indicated a very sudden *rise* in temperature to − 18°, while the background, which previously had been very dim, became brighter. A portion of the background came up so strong as to unite with and broaden each band on the violet side, thereby producing very broad flat bands of double the width of the original bands. This occurred after the phenomenon of under cooling. At the same time there was a five-fold increase in the intensity of the bands.

At − 46° the half of each band nearest the violet began to decrease in intensity while the other half grew brighter, which caused a marked decrease in the width of the bands. It was found by reversing the cooling process that the − 60° spectrum persisted while the temperature was raised to the cryohydrate point at − 18°, when it suddenly faded into the original dim spectrum. There was no suggestion of the broad flat bands at − 40° which were produced on cooling.

With the aid of the spectrophotometer it was again found that a marked increase in brightness had occurred; for the crests of the bands were 85 times as bright at − 60° as at + 20°. It will be noted, by referring to Fig. 4, that the bands doubled at − 90°, and that a dim intermediate series of bands appeared. Subsequent cooling increased the resolution of the doublets without shifting them very much, and also produced a few new bands. At − 180° the doublets were 85 + frequency units apart and formed two series; the unresolved red band being a member of one series and the blue band at 4,855 A. u. a member of the other. The very dim intermediate bands formed two different series, one of 85 and the other of 84 frequency units.

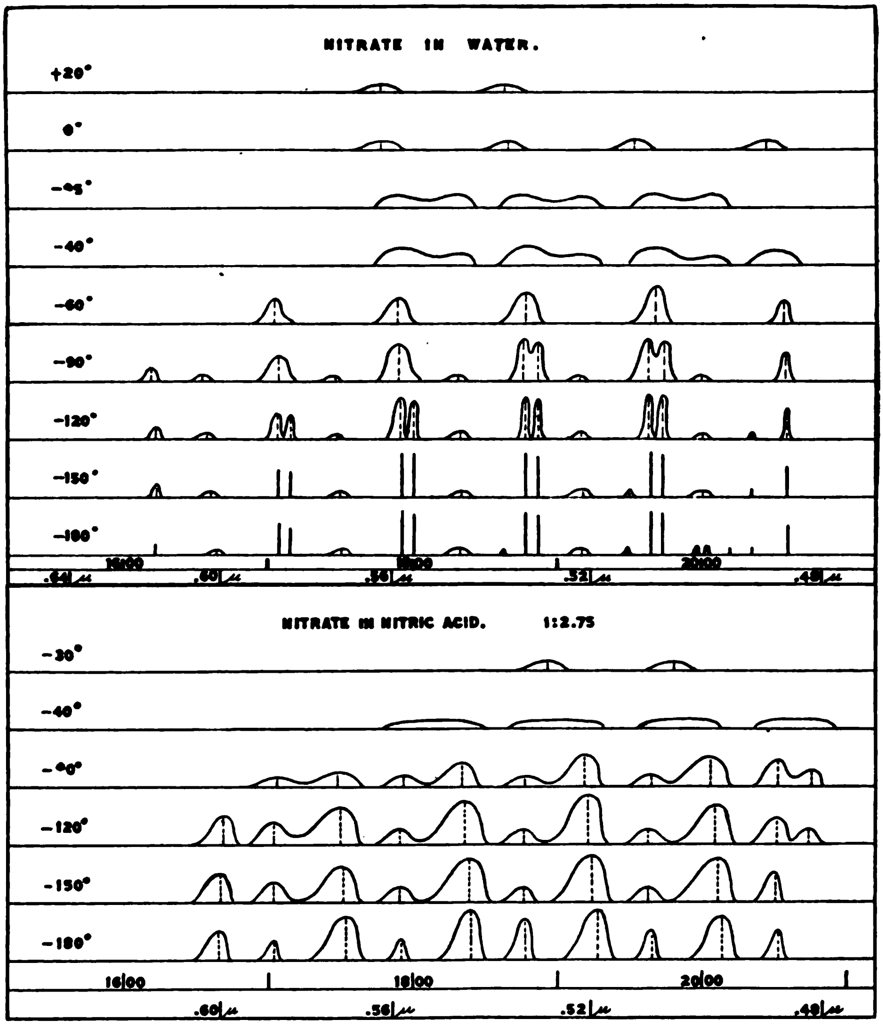

Fig. 4.

The 1/10 normal solution gave similar spectra when the temperature was lowered, but the resolution was not so complete.

The effect of further dilution with water can be seen in Fig. 5. The 1/1,000 normal solution shows single broad bands, considerably shifted with respect to the intermediate bands of the more concentrated solutions.

The 1/10,000 bands are in nearly the same positions as were the doublets of the normal solution.

Uranyl Nitrate in Nitric Acid.

The normal aqueous solution was almost unaffected by small amounts of nitric acid, as a study of Fig. 6 will show. The spectrum at the top, marked 20 : 1, was produced by exciting to fluorescence a solution of 20 c.c. of the normal solution to 1 c.c. of acid, after it had been slowly cooled to liquid air temperature. The acid brings out more of the very dim bands, and tends to decrease the resolution of the strong doublets. There was no shift, or marked change in resolution until the spectrum of the 1 c.c. of solution to 2.5 c.c. of acid mixture was observed. In the next spectrum, 1 : 2.75, a striking increase in intensity of the broad dim bands was noticed, while the doublets were replaced by single bands. The spectra of these two solutions at higher temperatures are shown in Figs. 4 and 6.

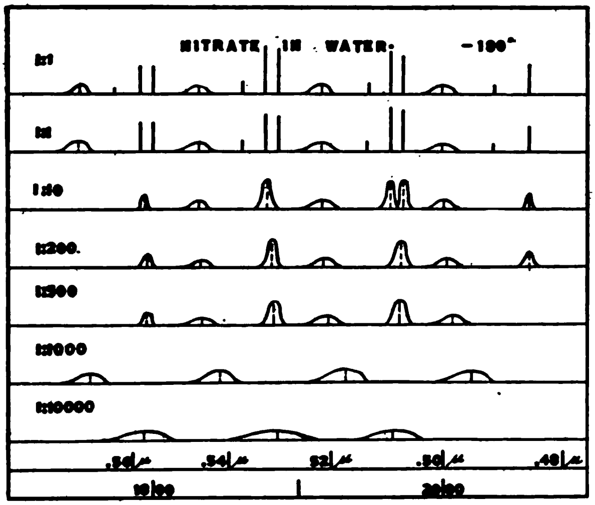

Fig. 5.

The spectrum following, that of a solution of one part normal, aqueous, to five parts nitric acid, was of the same type as the 1 to 2.75 solution, but shifted twelve frequency units toward the violet. The *same spectrum persisted in the four dilute solutions which follow, even when there was only one part of the aqueous solution to one thousand parts of concentrated nitric acid.*

The effect of nitric acid on the spectra of more dilute aqueous solutions of the nitrate was to produce broad banded spectra similar to those we have just studied. Often unstable solutions resulted, so that it was found difficult to reproduce the spectra of such solutions. Nor was this phenomenon of obtaining two or more distinctly different spectra confined to the dilute aqueous solutions with nitric acid. The three spectra, at — 180°, shown at the bottom of Fig. 3 illustrate this point. The

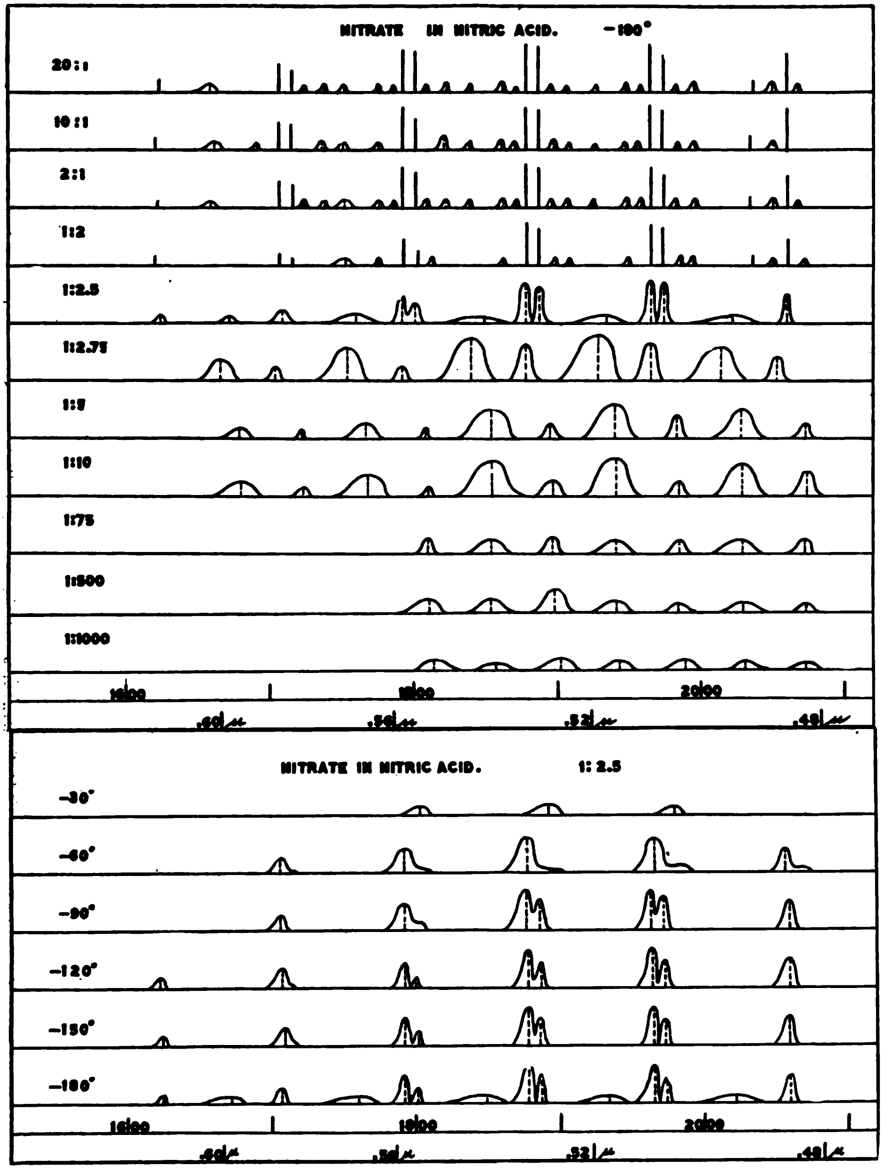

Fig. 6.

first two spectra, although entirely different, were produced from a solution of one part normal aqueous solution with ten parts nitric acid. The first spectrum was obtained after very slow cooling, the second, after a rather slow cooling, to liquid air temperature, but this second spectrum is identically the same as that obtained from a solution of one part normal to three and one half parts nitric acid when the usual slow cooling was employed. It was found that the 1 : 10 solution might give either spectrum under apparently the same conditions of cooling, in fact, it was somewhat accidental as to which spectrum would appear.

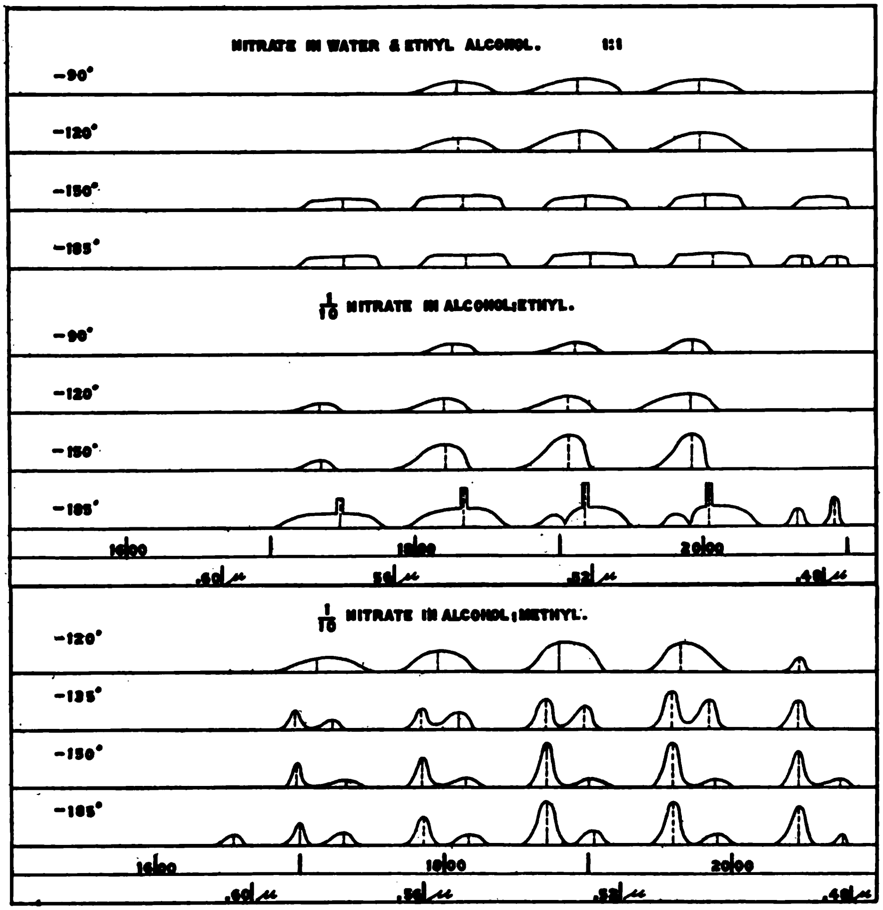

Fig. 7.

URANYL NITRATE IN ALCOHOL.

The fluorescence of an alcoholic and an aqueous normal nitrate solution, equal parts, showed an entire change in appearance from the spectrum of the aqueous solution. (See Fig. 7.) These bands occupied approximately the same positions as the intermediate bands of the normal nitrate in water at − 180°; but were broader and much less intense. The strong doublet series of the aqueous solution appeared to be entirely quenched by the alcohol. The frequency interval is the same for this solution as for the aqueous solution.

Another alcoholic solution was made by dissolving uranyl nitrate crystals directly in ethyl alcohol. (See Fig. 7.) The bands shifted toward the red at − 120°, and drifted toward the violet until − 150° was reached, when they began to shift back rapidly toward the violet while the crests protruded in a striking manner. It is important to note that these sharp crests are in the same positions at − 185° as the bands of the nitrate in water and ethyl alcohol.

A solution of the uranyl nitrate in methyl alcohol (see Fig. 7) gave series which both in manner of doubling and appearance closely resembled the aqueous solutions. The stronger members of the doublets are nearly in the same positions as the narrower members of the doublets of the quickly frozen aqueous solution (see Fig. 3), but the dim broad bands are shifted very decidedly toward the red in comparison with the positions of the broad bands of the aqueous solution. The doublets of the methyl alcohol solution also formed two series of bands with a constant frequency interval.

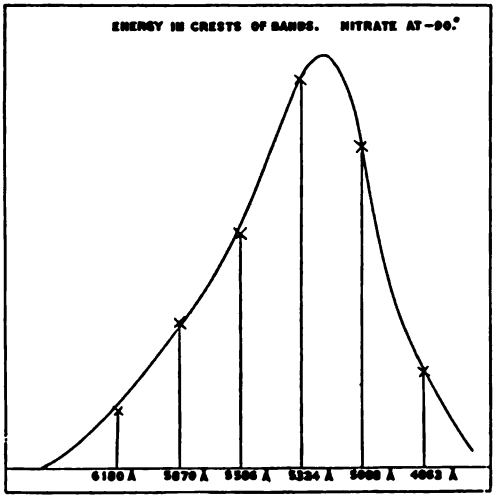

Fig. 8.

Distribution of Energy in the Bands of Uranyl Nitrate.

By the aid of a Hilger spectrophotometer, the brightness of the crests of the bands was compared with the brightness of the acetylene flame spectrum. These values were multiplied by the ordinates of the corresponding wave-lengths of the energy curve for acetylene.[1] (See Fig. 8.) Nichols and Merritt[2] found such a curve for the distribution of energy in the bands of several of the uranyl salts at room temperature, as well as for the distribution of energy throughout the spectra.

SUMMARY AND CONCLUSIONS.

The changes produced in the spectra of the aqueous solutions of the uranyl salts by slowly lowering the temperature from room temperature to liquid air temperature are:

1. A proportionate increase in the intensity of all of the bands.
2. A shift either toward the red or the violet.
3. A narrowing of the bands and in some solutions a tendency towards resolution.
4. A slight change in the frequency interval between bands, although it appears to be constant at any given temperature. The only exception to this statement is the fact that occasionally an extreme red or blue band does not join the constant interval series.

A suddenly cooled solution of the uranyl nitrate has a different spectrum from the same solution when slowly cooled. This is also true of the double nitrates.

Dilution with acid produces larger shifts than dilution with water and often radically changes the appearance of the bands.

The alcoholic solutions are invariably dim and broad-banded, and offer a less interesting field for investigation than the aqueous solutions.

The fact that two or more different spectra can be obtained from the same solution of the nitrate may be explained by assuming that when a radically different spectrum is produced a different hydrate is formed.

The extraordinary shifts and other changes in the spectra recorded are most readily explained by assuming, as has been done in the case of a study of the fluorescence and absorption spectra of the uranyl salts recently completed by Professors Nichols and Merritt and to be published shortly in the PHYSICAL REVIEW, that the bands in such spectra are complex, and consist of overlapping components, which vary relatively in intensity with changes in temperature.

Many thanks are due to Professors Nichols and Merritt and other members of the staff for the interest that they have taken in this work.

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[1] Coblentz, Bur. of Standards, Vol. 7, No. 2, p. 259.

[2] PHYSICAL REVIEW, Vol. XXXII., p. 358.

CHARGED SURFACE LAYERS FORMED ON THE ELECTRODES OF VACUUM TUBES.

By K. T. Compton and L. W. Ross.

Introduction.

Several years ago one of the writers observed that metals which had been used as cathodes in an X-ray discharge, in the attempt to obtain fresh clean surfaces, exhibited abnormal and very erratic photoelectric properties. In some cases the emitted electrons appeared to possess extremely high velocities while in other cases a strong field in addition to the action of the light was required to free the electrons from the surface. A later investigation[1] showed that such apparently abnormal photoelectric velocities, which had been observed by several investigators, were due to some sort of surface phenomenon which had the effect of greatly changing the contact difference of potential between the emitting and receiving electrodes and thus exposing the electrons to a strong accelerating or retarding field. Recently Seeliger[2] has found evidences of an electrical double layer, formed on the cathode of an X-ray bulb, which has the effect of changing the normal potential of the cathode by about 3 volts.

Because of the frequent use in research of metallic films sputtered from cathodes and of metals which have been exposed to X-ray discharges it is of practical importance as well as theoretical interest to understand the nature of this surface phenomenon, the cause of its erratic behavior and the methods by which it may be controlled.

For the experimental investigation we employed the following apparatus. Enclosed in the brass cylindrical vessel *MN* were the disk-shaped plates *P* and *B*, of platinum and brass respectively, which served as the electrodes for the vacuum discharge. The vessel could be opened at *FF*, where the upper part fitted into an accurately ground groove cut in the base and around which wax was melted to render the joint airtight. The vacuum was maintained by a Gaede pump connected to the vessel by the brass tube *A*.

The effect of X-ray discharges on the nature of the surfaces of the plates *P* and *B* was determined by measurements of the contact difference of potential between the opposing surfaces of these plates. These measurements were made by Kelvin's method.[3] The plate *P* could be moved up or down by turning the ground-glass joint J_1 and this formed, with *B*, a parallel plate condenser of variable capacity. The plate *B* was connected with a quadrant electrometer *E*. When the potential of the plate *P* was adjusted by the potentiometer *S* so that no deflection of the electrometer was observed when the plate *P* was raised or lowered, then the voltmeter *V* indicated the contact difference of potential between *P* and *B*.

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[1] Otto Stuhlmann and Karl T. Compton, Phys. Rev., Vol. 2, p. 199 (1913).

[2] Phys. Zeit., XIV., p. 1273 (1913).

The plate *B* was so large (6 cm. diameter) as to leave only one millimeter clearance between it and the vessel *MN*. During each X-ray discharge the plate *B* and the vessel *MN* were earthed and the plate used as anode or cathode as desired. In this way the lower side of the plate *B* was shielded from the effects of the discharge. By rotating the ground-glass joint J_2 the plate could be reversed and its shielded face tested for contact potential.

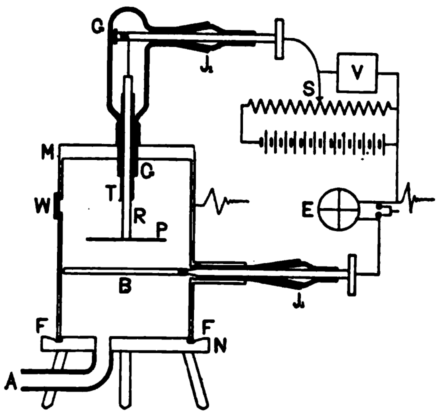

Fig. 1.

The sensitiveness of the system was such that one volt difference of potential between *B* and *P* caused a deflection of about 40 millimeters when the plate *P* was raised or lowered. In most of the work quickness rather than high accuracy was desirable.

EXPERIMENTS WITH CLEAN SURFACES.

For the first tests the inside of the vessel was rendered as free as possible from wax and insulating materials. The inside of the vessel and all metal parts were vigorously polished with emery and tripoli powders and wiped clean. All insulation on the inside of the vessel was shielded from the direct discharge and so disposed as to reduce to a minimum effects due to charges accumulated on the insulation.

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[3] Lord Kelvin, Phil. Mag., Vol. 56, p. 82 (1898).

Under these conditions we passed discharges of various durations between the plates *P* and *B*, using *P* as the cathode, and measured the contact difference of potential after each discharge. Some typical results are indicated in Table I. The contact difference of potential is called positive when of the normal sign, *i. e.*, brass positive with respect to platinum. Evidently the discharge produces a very slight disturbance in the contact difference of potential. A comparison of these results with others in which less care was taken to eliminate wax from the vessel indicates that these are due to slight traces of wax (possibly due to the vapor pressure of the wax in the joints) remaining in the vessel in spite of the efforts made to avoid them.

Table I.

Duration of Discharge.	Contact Potential.	Duration of Discharge.	Contact Potential.
0 sec.	0.30 volt	80 sec.	−0.25 volt
2	0.21	140	0.00
12	−0.04	440	0.15
20	−0.23	1,040	0.12
40	−0.25	1.940	0.06

Experiments with Insulating Films.

The effect is on the wax film. When films of various kinds of wax were placed on the plate *P* and this plate was used as anode or cathode, the apparent values of the contact difference of potential after the discharges varied between ± 500 volts and the value in every case was unchanged by reversing the plate *B* and testing with its shielded side opposed to *P*. But when the plate *P* was cleaned and wax was placed on the upper side of the plate *B* it was found, after each discharge, that the high contact difference of potential between *B* and *P* entirely vanished when the clean side of *B* was placed opposite *P*. These tests show conclusively that the abnormal contact potentials are due to and exist in the insulating films.

The effect of reversing the plate was as here described only provided the discharge had not been excessively heavy and long. It was found that very heavy discharges vaporized the wax, which condensed all over the inside of the apparatus and vitiated the above tests.

The nature of the effect depends on the conditions of the discharge. We found that the nature of the effect did not depend appreciably on the degree of vacuum, within wide limits, but that it was determined jointly by the time and the intensity of the discharge. Typical sets of measurements are shown in Table II. The effect on the wax film of a short discharge or of a weak one is to leave the outer surface of the film coated with an electrified layer of sign opposite to that of the waxed plate during the discharge. A long and heavy discharge reduces the intensity of electrification of the layer and may even reverse the sign.

TABLE II.

Discharge.		Contact Potential. Soft Wax on		
Time.	Nature.	Pt. Cathode, Volts.	Pt. Anode, Volts.	Brass Anode, Volts.
Before............	Sputtering	0.40	0.40	0.40
0.5 sec............	Weak	−120	35	− 75
Several 0.5 sec......	Medium	−160	130	−130
30 sec............	Heavy	− 50	− 6.5	− 60
30 sec............	Heavy	− 30	....	− 40
1 min............	Heavy	− 10	−13	− 12
1 min............	Light	−100	2	
1 min.	Heavy	− 45	− 6.5	
Several 0.5 sec......	Heavy	−160	75	−100
15 min...........	Heavy	2	−11	− 2

These contact potentials decay with time. A typical rate of decay curve is shown in Fig. 2, in which the waxed plate *P* was the anode. This change is initially much too rapid to be represented by a logarithmic curve. The largest values in Table II. are evidently not the maximum values since the measurements could not be made instantaneously

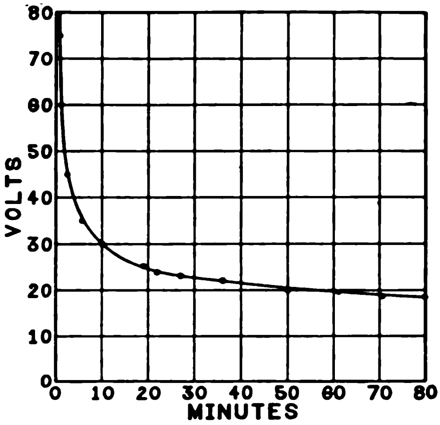

Fig. 2.

after shutting off the X-ray discharge. The rate of decay was distinctly more rapid in air than if a good vacuum was maintained.

Discussion of the Results.

These results are consistently and reasonably interpreted as due to two processes which are effective during the discharge. The first of these is the deposition of a layer of gaseous ions over the outer surface of the insulating film and the second is a convection current in the wax itself, whereby charged portions of the viscous wax are repelled from the metal to the outer surface. Obviously these two processes tend to give rise to contact potentials of opposite sign and the one which predominates depends on the nature of the discharge. We should expect the latter effect to be relatively important when the wax is heated and thus rendered less viscous. This was actually the case, for in Table II. we noticed that long and heavy discharges, which warmed the wax, produced effects of the latter sort. Short, light discharges on the contrary, produced strongly charged layers of sign opposite to that of the plate during the discharge.

In this connection it is significant that the largest effects due to convection currents in the wax occurred when the wax was on the anode, subject to the intense heat developed by the bombarding cathode rays. In this position only was the sign of the resultant potential easily reversed by long heavy discharges. It is also significant that long heavy discharges produced relatively larger effects when the wax was on the platinum plate than when it was on the brass plate, for the platinum plate was thin and of comparatively small heat capacity and its temperature was more easily raised by the discharge. In every case in which the reverse effect was marked evidences that the wax had been strongly agitated during the discharge were noticed when the apparatus was taken apart. This roughening of the surface was not noticed after short or light discharges.

This explanation of the phenomena is strongly supported by experiments in which sealing wax and stopcock grease were substituted for the soft wax on the electrodes. We should expect, in the case of sealing wax, that the effect due to the deposited ions would strongly predominate and that, because of the high viscosity, the maximum contact potential would be larger and the rate of decay smaller than in the case of soft wax. In the case of stopcock grease we should expect the contrary peculiarities.

We found, with sealing wax, contact potentials larger than 500 volts in the direction to be accounted for by deposited ions. The rate of decay was very slow. Only once, after a very heavy discharge, did we find a reversal of sign in the contact potential. In this case the wax had been melted by the discharge. With stopcock grease the highest measurement recorded was 21 volts and most values were about 5 volts. We also found that reverse effects, *i. e.*, contact potentials of the same sign as the applied potential, were observed even after applying potentials too small to produce a vacuum discharge, for instance 150 volts. In all cases the rate of decay was very rapid.

CONCLUSIONS.

1. The abnormal contact potentials produced on the electrodes by high potential discharges are due to and exist in insulating films such as wax or grease on the surfaces of the electrodes and are reduced or eliminated by shielding or avoiding all such substances.

2. On insulating films of small viscosity surface charges are produced by convection currents in the film set up by the applied field, even though this field may be too small to produce a vacuum discharge.

3. During a vacuum discharge a charged layer of gaseous ions is deposited on the surface of the insulating film. This charge is of a sign opposite to that of the potential of the electrode during the discharge and is therefore opposite to that produced by convection currents.

4. The apparent contact difference of potential is the resultant of these two effects, whose relative importance depends on the viscosity of the film and the nature of the discharge.

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AN ATTEMPT TO DETECT A CHANGE IN THE HEAT CONDUCTIVITY OF A SELENIUM CRYSTAL WITH A CHANGE IN ILLUMINATION.

By L. P. Sieg.

Introduction.—The fact that selenium changes its electrical conductivity so markedly with illumination has no doubt led many investigators to consider the possibility of a change in its heat conductivity with a change in the illumination. This has been of especial interest since the development of the electron theories for both kinds of conduction. However, careful search has revealed but one paper; that by Bellati and Lussana[1] bearing directly on the subject. These authors worked with a thin disc of crystallized light-sensitive selenium. The disc was painted with a thin coat of the red double iodide, Cu_2I_2, HgI_2. This substance turns chocolate brown at about 70° C. and so the color serves as an indicator of the extent on the disc where the above temperature has been attained. They heated a point of the disc with an electrically heated platinum wire. In the sunlight the increase in the thermal conductivity over that in the dark amounted, in one case cited, to about ten per cent. They noted further that the percentage change in the thermal conductivity agreed well with the percentage change in the electrical conductivity where exposure was made to the same light.

Some experiments of my own, performed on a selenium crystal are in serious disagreement with the above conclusions, and are here presented.

Theory of the Experiment.—It seems very questionable whether any simple electron theory is capable of explaining the light electric actions in selenium. Even assuming constant illumination one should be slow to adopt any of the standard electron formulas for heat and electric conduction. Lorentz,[2] Drude,[3] Livens,[4] Thompson,[5] Wilson,[6] and others have developed electron formulas for thermal and electrical conduction in metals. It will not be necessary to repeat these formulas here. It is to be noted, however, that although these formulas differ in the constants involved, they agree in the essential matter that the ratio of the electrical to the thermal conductivity is a function of the temperature, and is independent of the number of free electrons, their velocities, or their mean free paths. The classic experiments of Jaeger and Disselhorst[1] have given ample experimental verification of this independence. One might expect then that any agency that increases the electrical conduction of selenium, might be expected to increase in a measure the thermal conduction. To be sure we should not expect to find as large an increase for the thermal conductivity as for the electrical conductivity, for selenium is at best a very poor conductor of electricity, and so doubtless a large share of the heat conduction is by means of atoms and molecules, just as is true in the case of electric insulators. Nevertheless, if under the action of light there are more electrons *actually made free*, or if those free have a *greater mean velocity* or *path*, there should be at least a small increase in the thermal conductivity. The experimental results described below show, however, that if there is any such improvement in the heat conductivity it is smaller than the error of these measurements.

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[1] Atti del R. Inst. Ven. (6), 5, 19, 1887. Abs. Beib. d. Ann., 11, 818, 1887.

[2] Theory of Electrons, pp. 67, 266.

[3] Ann. d. Phys., 1, 566, 1900; 3, 369, 1900.

[4] Phil. Mag., 29, pp. 173, 425, 1915.

[5] Phil. Mag., 14, 217, 1907.

[6] Phil. Mag., 20, 835, 1910.

Apparatus and Method of Observation.—A modified form of the apparatus described many years ago by Christiansen[2] was used. A form of apparatus was required that would meet several conditions. It was decided to work with an isolated crystal of selenium.[3] It was necessary that the apparatus serve to obtain the heat conductivity and the electrical conductivity both in the dark and in the light, and further if possible that it should serve to get the variation of the above quantities with the temperature. A reference to the figure will make the following description clear. At the base is a brass cylinder through which passes a stream of cold water. This cylinder is about 50 mm. in diameter by 20 mm. high. On top of this are placed in succession the following layers. Outside, and in the form of washers we have, a copper plate, a glass plate, a copper plate, a glass plate, and a copper plate. Inside, and in the form of small discs we have the following five layers: a copper disc, a glass disc, a copper disc, a selenium crystal, and a copper disc. The total height of all five discs is 4.5 mm. The other necessary dimensions are indicated on the figure. The purpose of the outside washers was to form a guard ring having about the same temperature gradient as is to be found in the central pile of discs. The various washers and discs were joined together with thin films of glycerin in order to improve the heat conductivity of the junctions. Above the whole is an electric heater. In practice this was separated from the top copper disc and washer by thin cover glass for purposes of electric insulation. Thermo-couples end in the central copper discs, the wires passing through the outer washers as shown, and insulated from them. The solid lines indicate copper wires and the dot and dash lines constantan wires. The

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[1] Preuss. Akad. Wiss. Ber. Sitzungsber., 38, 719, 1899, also Phys. Tech. Reich., Wiss. Abh. 3, 269, 1900.

[2] W. Ann., 14, 23, 1881.

[3] The crystal was kindly given to me by my friend Dr. F. C. Brown. The crystal was a close grown fern-like one made up of small, and very probably, hexagonal spines. For further description see PHYS. REV., Ser. 2, 4, 85, 1914.

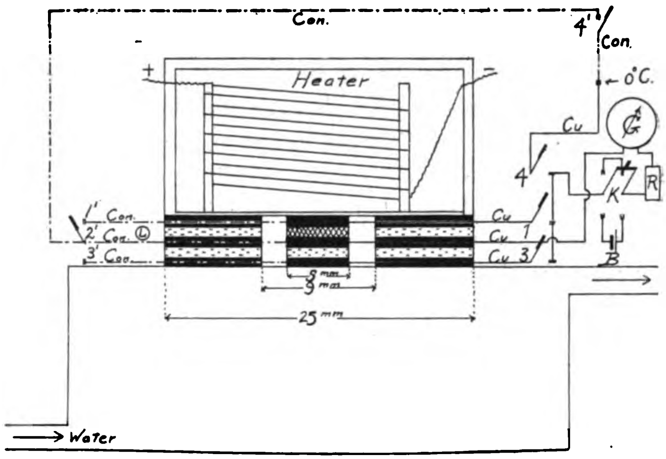

Fig. 1.

switches and other apparatus at the right clearly indicate the manipulations. When the key *K* is closed upward, the various thermo-couples can be thrown in series with the galvanometer so as to enable one to read the temperature difference between the middle junction No. 2 and any of the others, Nos. 1 or 3, or an outside couple, No. 4, the latter for purposes of calibration. For example if, with *K* closed upward, key No. 1 is closed and double throw key No. 2′ is connected with terminal, 1′, we have the thermo-couple copper-constantan in series with the galvanometer and the resistances *R* with the hot (usually) junction in the top copper disc, and the cooler junction in the middle disc. There is an electrical by pass in this circuit, viz., the conduction through the selenium crystal between discs No. 1 and 2, but considering that the whole resistance of the thermo-couple circuit, including the galvanometer, was only about 40 ohms and that the resistance of the crystal was over 1,000,000 ohms we see that no measurable error could enter. If all the keys are opened but No. 1, and *K* is closed downward, then a cell *B* is placed in circuit and the electrical conductivity of the crystal can be obtained by the galvanometer deflection. A 25-watt tungsten lamp placed at *L* could be thrown on or off at will. The light passed through the clear glass of the upper washer, thus removing much of the heat energy, and so illuminated the selenium crystal. The illumination was sufficient to increase the equilibrium electrical conductivity at ordinary room temperature to nearly three times the dark conductivity.

The theory of the experiments rests on the assumption that the heat that enters the top copper disc passes on down through the pile of discs without loss and is ultimately delivered to the cooling water. In the original method Christiansen used three flat discs with imbedded thermometers and attempted to keep the middle copper disc at room temperature. In this improved guard ring method, if there is about the same temperature gradient between heater and cooler through the discs and the inside of the washers, then there should be no lateral gain or loss of heat so far as the central discs are concerned. If the temperature of the top copper disc is taken as T_1, of the middle one T_2 and of the bottom one T_3, if the thickness of the selenium crystal is d_1 and of the glass disc is d_2, if their thermal conductivities are represented by K_1 and K_2 respectively, and lastly if we assume that the quantity of heat H that enters the top disc likewise leaves the lowest one,

$$H = K_1\frac{(T_1 - T_2)A\cdot t}{d_1} = K_2\frac{(T_2 - T_3)A\cdot t}{d_2}.$$

Since the time of flow, t and the areas of the discs, A are the same, we get

$$\frac{K_1}{K_2} = \frac{T_2 - T_3}{T_1 - T_2}\cdot\frac{d_1}{d_2},$$

or with constant thickness of the two discs,

$$\frac{K_1}{K_2} = C\frac{T_2 - T_3}{T_1 - T_2},$$

where C is a constant.

We are thus able to obtain, not the absolute thermal conductivity of the selenium crystal, but rather its ratio to that of glass. For absolute measurements a correction would have to be made on account of the fact that we assume the temperatures of the copper plates to represent the true temperatures of the two sides of the crystal and of the glass respectively. Christiansen gives the necessary correction formulas.[1] In the present investigation no attempt has been made to obtain the absolute thermal conductivity of the selenium crystal. This is because the other question was of paramount interest, and because, on account of the small interstices of the crystal, one would have had to make careful corrections for the heat transmitted by radiation. However, the apparatus is extremely sensitive and reliable for these comparison measurements.

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[1] Loc. cit.

The procedure was as follows: The tap water had been running for some hours until it had reached a steady temperature. The heater was left at room temperature in a room, the temperature of which held within a degree during any one set of experiments. After equilibrium had been attained, usually in ten to twenty minutes, the galvanometer readings for $T_1 - T_2$, $T_3 - T_2$, and $T_4 - T_2$ were obtained. T_4 was the temperature of the extra junction and was used for calibrating the couples so that galvanometer readings could be reduced to degrees Centigrade. All these readings were taken in a dimly lighted room. The electrical conductivity of the selenium was then obtained by closing key No. 1 and key K downward. The lamp L was now lighted, and after about twenty minutes similar readings were again made. While these readings were being reduced a small current was turned on through the heater. After equilibrium the process was repeated, and so on with various temperature gradients. Typical results of such a set of experiments are found in the table. The galvanometer deflections are for brevity not included. The first six columns are self-explanatory. The seventh represents roughly the mean temperature of the selenium. The column headed C gives the galvanometer deflections and hence a measure of the electrical conductivity of the selenium. The column headed k_1/k_2 × constant, gives a measure of the relative conductivity of the selenium as compared with the glass. The latter has an unknown, but undoubtedly small temperature coefficient. R is the ratio of the electrical conductivity of the selenium in the light to that in the dark. The last column is self-explanatory. Further examination of the table will make it clear that the ratio k_1/k_2 is not modified by changing from the light to the dark for any given temperature. This means of course, if we assume the light to have no appreciable effect on the thermal

T_1-T_2	T_3-T_2	T_4-T_2	T_1	T_2	T_3	$T_1+T_2/2$	C	k_1/k_2 × Const.	R	State of Selenium.
10.9	− 3.3	6.7	27.2	16.3	13.0	21.8	27	.34	2.48	dark
10.9	− 3.4	6.3	27.6	16.7	13.3	22.1	67	.35	......	light
12.5	− 4.1	3.7	31.8	19.3	15.2	25.6	33	.37	2.12	dark
12.8	− 4.2	3.7	32.1	19.3	15.1	25.7	70	.37	......	light
19.4	− 7.1	− 2.3	44.7	25.3	18.2	35.0	41	.39	1.75	dark
19.5	− 7.2	− 2.6	45.1	25.6	18.4	35.4	72	.39	......	light
27.9	− 9.8	− 7.7	58.6	30.7	20.9	44.7	45	.36	1.67	dark
28.2	−10.4	− 7.7	58.9	30.7	20.3	44.8	75	.38	......	light
46.1	−17.5	−19.8	88.9	42.8	25.3	65.9	53	.39	1.55	dark
46.4	−17.5	−19.2	88.6	42.2	24.7	65.4	82	.38	......	light
61.7	−23.8	−28.8	113.5	51.8	28.0	82.7	92	.39	1.28	light
61.7	−24.4	−29.4	114.1	52.4	28.0	82.3	72	.40	......	dark
73.8	−29.1	−37.4	134.2	60.4	31.3	97.3	72	.40	......	dark

conductivity of the glass, that it has no appreciable effect on the thermal conductivity of the selenium. There seems to be a slight increase in the ratio of k_1/k_2 wtih higher temperatures, but whether this is due to a decrease of the conductivity of the glass used, or an increase in the conductivity of the selenium, or both is impossible to state. If one had at his command a glass, the temperature coefficients of which were known, then he could settle this point.[1]

Incidentally, although the investigation was not directed toward this point, one notes that the electrical conductivity of the selenium both in the dark and in the light increases with increased temperature, but that the ratio of the two decreases. In other words, the selenium while becoming a better conductor of electricity is becoming less light sensitive.

Conclusion.—There may be advanced perhaps a number of reasons why the thermal conductivity was not appreciably changed by the illumination. One might suppose that the number of free electrons is so very small (judging from rough estimates of specific conductivity, about 10^{-12} the number present in copper) that even if there were a threefold increase in their number by the action of the light, that still the number is too small to make an appreciable effect in the thermal conductivity. In other words, the heat conduction in a selenium crystal is largely a matter of the vibrating atoms and molecules.

Another possibility is to assume that the number of free electrons present is not solely determined by the state of light or dark, but is more largely determined by the electric field intensity. If this were so, then one could easily see how the electrical conductivity could be increased without a corresponding increase in the thermal conductivity. The electrons could be assumed to be in an unstable state within the atom, and under the action of the light the instability is increased, but still the electrons are not expelled until an electromotive force is applied. The fact that the resistance of these crystals, and also of selenium cells in general is lowered by increased potential is evidence along this line. The lowered resistance can be interpreted as representing more actually freed electrons.

Whatever the explanation, the experimental results developed that whilst the given source of light increased the electrical conductivity nearly 300 per cent., the same light did not increase the thermal conductivity in any appreciable manner. Considering all possible sources of error, it must certainly have been under five per cent.

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[1] The glass used was supplied by Bausch and Lomb from their regular cover-glass stock.

THE PRINCIPLE OF SIMILITUDE AND THE PRINCIPLE OF DIMENSIONAL HOMOGENEITY.

By Richard C. Tolman.

THE writer has recently presented[1] a new postulate, called the principle of similitude, which serves as a successful starting point for the deduction of a considerable number of physical laws. There is a certain similarity between the methods of applying this new principle to the deduction of physical laws and the methods of applying the well-known principle of dimensional homogeneity, and the purpose of the present article is to show, in the first place, *that the essential content of the two principles is in reality quite distinct*, and in the second place that it is *possible to derive important relations from the principle of similitude which cannot be derived from the principle of dimensional homogeneity and vice versa.*[2]

Statement of the Principle of Dimensional Homogeneity.—Let us first state the principle of dimensional homogeneity in such a form that we may later compare its essential content with the content of the principle of similitude.

All of the equations of mathematical physics can obviously be put in the general form

$$A' + B' + C' + \cdots + N' = 0, \tag{1}$$

where each of the letters A', B', C', etc., expresses some function of the magnitude of a property or a functional combination of the magnitudes of several properties. The principle of dimensional homogeneity requires that all the terms A', B', C', etc., shall have the same dimensions, in other words, that the equation itself shall be unaltered if we multiply every value of length in the equation by some arbitrary multiplier x, every time interval by another arbitrary multiplier y, every mass by z, etc., using a different arbitrary multiplier for each of the five fundamental properties, length, time, mass, permeability, and temperature.[1]

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[1] Phys. Rev., *3*, 244, 1914; ibid., *4*, 145, 1914.

[2] The writer has intended for some time to point out the exact relation and difference between the theory of similitude and the ordinary theory of dimensions. A more immediate necessity for the present paper, however, is to be found in an article by Dr. E. C. Buckingham on the use of dimensional reasoning. (Phys. Rev., IV., 345, 1914.) Dr. Buckingham intimates in the first place (p. 356) that the theory of similitude contains nothing foreign to the ordinary theory of dimensions, and in the second place (p. 357) that all the consequences of the theory of similitude can be obtained from the principle of dimensional homogeneity. We shall show, however, that such is not the case.

TABLE I.

Dimensions of a few Important Properties.[2]

Geometrical Properties.	**Dimensions.**
Length, l	$[l]$
Area, S	$[l^2]$
Volume, V	$[l^3]$
Angle, α	$[l^0]$
Kinematical Properties.	
Time, t	$[t]$
Velocity, v	$[lt^{-1}]$
Acceleration, a	$[lt^{-2}]$
Dynamical Properties.	
Mass, m	$[m]$
Density, ρ	$[ml^{-3}]$
Momentum, M	$[mlt^{-1}]$
Force, F	$[mlt^{-2}]$
Energy, U	$[ml^2t^{-2}]$
Energy Density, u	$[ml^{-1}t^{-2}]$
Pressure, p	$[ml^{-1}t^{-2}]$
Elasticity of compression, $E = V(dp/dV)$	$[ml^{-1}t^{-2}]$
Electrical Properties.	
Permeability, μ	$[\mu]$
Charge, e	$[m^{1/2}l^{1/2}\mu^{-1/2}]$
Inductivity, κ	$[l^{-2}t^2\mu^{-1}]$
Potential,	$[m^{1/2}l^{3/2}t^{-2}\mu^{1/2}]$
Capacity,	$[l^{-1}t^2\mu^{-1}]$
Current,	$[l^{1/2}m^{1/2}t^{-1}\mu^{-1/2}]$
Resistance,	$[lt^{-1}\mu]$
Electric field strength, E	$[l^{1/2}m^{1/2}t^{-2}\mu^{1/2}]$
Magnetic field strength, H	$[m^{1/2}l^{-1/2}t^{-1}\mu^{-1/2}]$
Thermal Properties.	
Temperature, T,	$[T]$
Entropy, S,	$[ml^2t^{-2}T^{-1}]$
Heat capacity,	$[ml^2t^{-2}T^{-1}]$
Specific heat,	$[l^2t^{-2}T^{-1}]$

In carrying out this multiplication, the values of derived properties will have to be multiplied by the proper combination of the arbitrary multipliers x, y, z, etc., corresponding to the dimensions of the derived property in terms of those chosen as fundamental. It should also be specially noticed that if any dimensional constants occur in the equation, such as the R in the gas law $pv = NRT$ or the a in Stefan's law $u = aT$, these too will have to be multiplied by the suitable combination of x, y, z, etc., in order for the equation to maintain its invariance.

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[1] For reference the dimensions of a number of important quantities are given in Table I. It was pointed out by Sir A. W. Rucker (Proc. Phys. Soc. Lond. (1888) 10, 37) that *five* fundamental properties are necessary for the treatment of our present body of physical knowledge, and the five used in the table are those most ordinarily chosen. In another place the writer will discuss a more rational choice of properties to be taken as fundamental.

[2] See any text on the dimensions of units, for example, Ency. Brit., 11th edit., article on "Units."

Method of Applying the Principle of Dimensional Homogeneity.—Let us now briefly consider the method of deducing physical laws from the principle of dimensional homogeneity so that we may later show the possibility of deriving laws from the principle of similitude that cannot be derived from the principle of dimensional homogeneity.

Considering equation (1), since all the terms in that equation must have the same dimensions, it is evident that if we divide through by $(-N')$ we shall obtain a new equation of the form

$$A + B + C + \cdots\cdots\cdot = 1, \tag{2}$$

where all the terms are now of zero dimensions. If now Q_1, Q_2, Q_3, etc., are quantities which express the values of the different properties whose quantitative interrelation is given by equation (2), each of the terms A, B, C, etc., will be some functional combination of these quantities. It is evident, moreover, that the only functional combinations of Q_1, Q_2, Q_3, etc., which will be of zero dimensions must be functions whose arguments are products of the general form

$$\pi = Q_1^{n_1}, Q_2^{n_2}, Q_3^{n_3}, \cdots, \tag{3}$$

where n_1, n_2, n_3, etc., are such integers that π itself is of zero dimensions. If now π_1, π_2, π_3, etc., are all the possible *independent* dimensionless products of this form, it is evident that we may rewrite equation (2) as follows

$$\phi(\pi_1, \pi_2, \pi_3 \cdots) = 1 \tag{4}$$

where ϕ may be any function.[1]

As a single illustration of the method of applying equation (4), suppose we wish to find the relation between the velocity of propagation v of a compressional wave in an elastic medium, the density of the medium ρ and its elasticity of compression $E = V(dp/dV)$. We have

$$[v] = [lt^{-1}], [\rho] = [ml^{-3}], [E] = [ml^{-1}t^{-2}]$$

and it is evident on inspection, that the only possible *independent* dimensionless product of these three quantities is $v^2(\rho/E)$ or some power of that combination. Substituting in equation (4) and solving for v we have a general expression for the velocity of a compressional wave

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[1] This equation is equivalent to Dr. Buckingham's Equation No. 9, *loc. cit.*

$$v = k\sqrt{\frac{E}{\rho}}, \tag{5}$$

where k is the same constant for all different media. The simplicity of the calculation by which we have obtained this important equation of elasticity theory is evident.

Limitations of Dimensional Reasoning.—Dimensional reasoning is very attractive because of its great simplicity. Nevertheless, it is only fair to point out its serious limitations.

An important limitation to dimensional reasoning consists in the fact that the equations arrived at by such considerations always contain numerical constants, such as the k in our equation for the velocity of wave motion, and the values of these constants must be obtained from other than dimensional sources, for example by experiment. When the same equations are derived from the specific considerations of the particular theoretical field in question, the values of these constants are usually obtained in the course of the calculation.

In the second place, we must notice that in order to carry out dimensional reasoning at all, we must either know or assume just what are the physical properties which we shall expect to find connected by a physical equation. Thus, if we know or assume that the velocity of a compressional wave depends only on the density and compressibility of the elastic medium, it is possible to derive the correct equation as we have done above. Unless we knew beforehand, however, something about the field of investigation, we might expect that the velocity of the compressional wave to depend on other properties of the elastic medium as well, for example its rigidity, and could thus be led to incorrect results.

For us, however, the most important limitation to dimensional reasoning arises in cases where, without the introduction of a ***dimensional constant***, no dimensionless product of the quantities involved is possible. A familiar example is provided by the equation connecting the pressure p, volume V, temperature T, and number of mols N of a perfect gas. The quantities involved are of the following dimensions $[p] = [ml^{-1}t^{-2}]$, $[V] = [l^3]$, $[T] = [T]$, and N the number of mols of gas may be looked upon as a pure number, which could be conceivable obtained by counting the number of molecules in the gas.

It is evident that there is no dimensionless product of these quantities since there is no way in which T can be cancelled out, and hence the principle of dimensional homogeneity will be of no assistance in predicting the form of the functional relation connecting them. The actual form of the familiar equation connecting the quantities is

$$pV = NRT \text{ or } \frac{pV}{NT} = R,$$

where R is the so-called gas constant. And in order that the equation shall agree with the principle of dimensional homogeneity we see that R must have the dimensions $[pV/NT]$, that is, of energy per mol per degree, *i. e.*, specific heat. Since, however, without a knowledge of the actual form of the equation there is no way to tell beforehand what the dimensions of such a constant would be, the principle of dimensional homogeneity is of no assistance in predicting the form of the equation. For example, if the gas laws were actually of the form,

$$\frac{p^3 V^{\frac{1}{2}}}{NT^3} = \text{constant},$$

we should merely have to assign to that constant the dimensions $[p^3 V^{\frac{1}{2}} N^{-1} T^{-3}]$ in order to agree with the theory of dimensions.

Another rather simpler example of the failure of dimensional reasoning to provide information as to the form of an important relation is furnished by the equation connecting the energy density u of a hohlraum and the temperature T. The dimensions of the quantities involved are

$$[u] = [ml^{-1}t^{-2}] \text{ and } [T] = [T],$$

and they permit of no dimensionless product. The actual relation between them is found to be

$$u = aT^4,$$

where a, the so-called Stefan's constant, must have the dimensions $[uT^{-4}]$ in order that the equation may agree with the principle of dimensional homogeneity. If the true relation, however, had turned out to be

$$u = aT^3$$

then a would have the dimensions $[uT^{-3}]$ and we see that dimensional reasoning gives us no assistance in predicting beforehand what the actual form of the relation is.

It is just in these cases where *dimensional constants* have to be introduced that the principle of similitude will sometimes come to our assistance, and permit a simple solution of problems that cannot be handled by ordinary dimensional reasoning. As we shall show, both of the examples considered above can be handled by the theory of similitude. In one case the theory provides a unique solution, and in the other prescribes important limitations to the actual form of the functional relation.

Let us now consider the content of the principle of similitude.

The Relativity of Size.—It is obvious that the numerical value obtained for the magnitude of any physical property which is capable of continuous variation will depend entirely on the magnitude of the unit chosen for the measurement. Thus the *numerical value* for the length of any object will be inversely proportional to the length chosen as a unit; the shorter we take our unit meter stick the more the number of times that we can fit it into the length of the object we are measuring.

Suppose now, however, that all objects in the universe should have their linear dimensions decreased in the ratio $1 : x$. Since the length of all our standards of measurement would be changed in the same ratio as all other lengths, it is evident that we should be unable to detect the change *by any ordinary process of measuring*, and this is what is meant by the idea of the relativity of size. When we speak of the length of a body, we really mean its length relative to some standard of measurement. If both the length of the body and the length of the standard of measurement should be suddenly changed in the same ratio, we should be unable to detect the change. Hence, we cannot speak of the *absolute* length of a body, but merely of the *relative* length of two bodies.

Although this principle of the relativity of lengths may seem very obvious it is not quite so simple as appears at first sight. This arises from the fact that there are other ways of estimating lengths besides that of counting the number of times the length of one object can be fitted into the length of another. For example, we might estimate the length of an object by noting the time it takes for a light signal to travel from one end of the object to the other. If now the length of our object were suddenly decreased, we should notice the fact since it would take a shorter time than before for light to travel from one end of the object to the other, *unless there should be a corresponding change either in the velocity with which light travels or in the rate of the clock which we are using to measure the time interval.* Now what we may call the idea of the *complete relativity of size* assumes the possibility of a coordinated change in the magnitudes of all measurable properties, lengths, time intervals, masses, temperatures, etc., of such a nature that no measurements of any description could lead to its detection. If such a coordinated change is possible, it will be meaningless to speak of the absolute size of any object in the universe.

The Principle of Similitude.—The idea of the *complete* relativity of size leads to the following statement of what may be called the principle of similitude: *The fundamental entities of which the physical universe is constructed are of such a nature that from them a miniature universe could* *be constructed exactly similar in every respect to the present universe.*[1] This principle may be regarded, if wished, as a perfectly arbitrary postulate from which we shall deduce conclusions that may then be compared with the actual relations in the physical world.

The Transformation Equations.—Consider two observers O and O' provided with instruments for making physical measurements. O is provided with ordinary meter sticks, clocks, and measuring apparatus of the kind and size which we possess in our actual universe U. O', however, is provided with a shorter meter stick, and correspondingly altered clocks, standards of mass and other measuring apparatus so that he can make measurements in a miniature universe U', which, in accordance with the principle of similitude, is so constructed that he obtains the same numerical results in all his experiments as does O in the analogous measurements made in universe U.

We shall be most particularly interested now, not in the measurements which O and O' could make each in an entirely separate universe, but in the relation between the results which they obtain when each makes measurements of the same physical phenomenon.

Suppose, for example, O and O' both measure the length of the same object and obtain respectively the values l and l'. Then if O''s meter stick is shorter than O's in the ratio of $1:x$, the numerical value l' will obviously be greater than l in accordance with the equation

$$l' = xl.$$

In the first of the articles already referred to (loc. cit.) it was found possible to obtain a whole series of transformation equations of the type

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[1] Ideas somewhat similar to that expressed by the principle of similitude have been considered in the past. Thus Newton, Lib. II., prop. 32, considers two similar dynamical systems, in which the particles are subjected to a *special law of attraction* and shows that if the two such systems are started with a similar configuration and state of motion, the particles will continue to move among themselves in each system with like motions and in proportional times; and Helmholtz, Jour. für Math., 97, 319, 1884, has shown that for systems which obey Lagrange's equations of motion, corresponding to any state of motion, another state of motion could be obtained in which all the velocities are increased x-fold provided the external forces are increased by a factor x^2. There have also been a number of considerations on the basis of dimensional reasoning as to the corresponding behavior of animals or other physical systems which are similar in form, but of different size. The essential content of the principle of similitude, as stated above, seems to be entirely new, however, and we find, moreover, that the development of a complete theory of similitude is dependent on new ideas quite recently introduced into physics by the Einstein theory of the relativity of motion and by the electron theory, since the development makes use of the principle of the unalterable constancy of the velocity of light in free space and of the indivisibility and fundamentality of the charge of the electron as the natural unit quantum of electricity.

Note Added July 30, 1915.—The phrase principle of similitude has also recently been used by Rayleigh (Nature, March 18, page 67, 1915) to denote what I have called in accordance with common usage the principle of dimensional homogeneity.

TABLE II.

Transformation Equations.

Length,	$l' = xl$
Area,	$S' = x^2 S$
Volume,	$V' = x^3 V$
Time interval,	$t' = xt$
Frequency,	$\nu' = x^{-1}\mu$
Velocity,	$v' = v$
Acceleration,	$a' = x^{-1}a$
Mass,	$m' = x^{-1}m$
Density,	$\rho' = x^{-4}\rho$
Force,	$f' = x^{-2}f$
Pressure,	$p' = x^{-4}p$
Elasticity of compression,	$E' = x^{-4}E$
Energy,	$U' = x^{-1}U$
Energy density,	$u' = x^{-4}u$
Electrical charge,	$e' = e$
Entropy,	$S' = S$
Temperature,	$T' = x^{-1}T$

$l' = xl$, connecting the measurement made by O and O' of given lengths, time intervals, masses, forces, charges, etc., and in Table II. we present such a series of equations for future reference.[1]

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[1] In deriving the transformation equation for absolute temperature, the writer inadvertently stated that absolute temperature had the same dimensions as energy. This is incorrect as was pointed out by Dr. Buckingham (*loc. cit.*). See, however, Lewis and Adams, PHYS. REV., III., 96, 1914, and Planck, "Vorlesungen über die Theorie der Wärmestrahlung." What the writer had in mind at the time was that since absolute temperature is proportional to the energy of the molecules of a monatomic perfect gas, the transformation equations for energy and for temperature must be the same. For example, consider the measurements of the temperature of a system which could be obtained by O and O' from observations of the mean kinetic energy of the molecules of a perfect gas which has been placed in thermal contact with the system in question. It is evident from the transformation equation for energy that these mean values of the kinetic energy will be connected by the relation $U' = x^{-1}U$ and hence since absolute temperature is proportional to the mean kinetic energy of such molecules our transformation equation for temperature must be

$$T' = x^{-1}T.$$

Another method of deriving the transformation equation for temperature would be to consider first the transformation equation for entropy. This is perhaps a more rational method of attack since we shall not need to consider the special properties of a perfect gas and shall hence feel more free to use our transformation equations in deriving the properties of a perfect gas.

Consider an *isolated* physical system which can exist in two different states (1) and (2). In accordance with the Boltzmann-Planck ideas as to the relation between entropy and probability we may write the equation

$$\Delta S = k \log \frac{W_2}{W_1}, \tag{1}$$

where ΔS is the increase in entropy when the system passes from state (1) to state (2), k is a universal constant and W_2/W_1 is the ratio of the respective probabilities of state (2) and state (1).

Method of Applying the Principle of Similitude.—The principle of similitude may be used to obtain information as to the form of the functional relation connecting the measurements of the properties of certain kinds of physical systems, namely, systems which might equally well form part either of universe U or of universe U' and would appear to have the same general nature in either universe. For such systems we may write the equation

$$F(Q_1, Q_2, Q_3, \cdots) = 0, \tag{6}$$

for the relation between the various measurements as made by O, or

$$F'(Q_1', Q_2', Q_3', \cdots) = 0, \tag{7}$$

for the relation between the measurements of the same properties as made by O'. Since, however, we are dealing with systems which have the same general nature in the two universes, it is evident from the

We may suppose that the quantities in equation (1) were measured by observer O. It is evident, however, that the system would also appear as a thermodynamic system to observer O' and hence his measurements would also have to obey the laws of thermodynamics in accordance with the equation.

$$\Delta S' = k' \log \frac{W_2'}{W_1'}. \tag{2}$$

It is evident from the principle of similitude, however, that the universal constant k' belonging to the miniature universe U' must be equal to the constant k in universe U. It is also obvious that W_2/W_1 is equal to the ratio which would be found by O for the relative lengths of time that the isolated system actually exists in states (2) and (1), while W_2'/W_1 is the same ratio as determined by O', which makes it evident that W_2/W_1 and W_2'/W_1 must be equal. We thus see that the quantities on the right hand sides of equations (1) and (2) are equal and hence obtain as the transformation equation for entropy

$$\Delta S' = \Delta S. \tag{3}$$

To obtain the transformation equation for temperature we may consider the equation

$$\Delta S = \int \frac{dQ}{T} \tag{4}$$

connecting the increase in entropy which accompanies a reversible change in the state of a system with the heat absorbed and the temperature of absorption. Since a reversible change in the state of a thermodynamic system would obviously appear to O' as well as to O to be reversible we may write for O''s observation of this same phenomenon

$$\Delta S' = \int \frac{dQ'}{T'}. \tag{5}$$

Now for $\Delta S'$ we may substitute ΔS in accordance with equation (3) and for dQ' which is a quantity of energy we may substitute $x^{-1}dQ$ in accordance with transformation equation for energy giving us

$$\Delta S = \int x^{-1} \frac{dQ}{T'},$$

and combining with (4) we have

$$\int x^{-1} \frac{dQ}{T'} = \int \frac{dQ}{T},$$

so that the transformation equation for temperature must be as we found before

$$T' = x^{-1}T.$$

principle of similitude that F and F' must be the same function, hence we shall be able to write

$$F(Q_1, Q_2, Q_3, \cdots) = F(Q_1', Q_2', Q_3', \cdots) = 0 \tag{8}$$

as a true equation. Our table of transformation equations, however, provides us with equations for all the Q''s in terms of the Q's, these equations being of the general form $Q' = x^nQ$. Substituting in (8) we obtain

$$F(Q_1, Q_2, Q_3, \cdots) = F(x^{n_1}Q_1, x^{n_2}Q_2, x^{n_3}Q_3, \cdots) = 0 \tag{9}$$

as an equation which will help us to determine the form of the functional relation F connecting the measurements of the various properties $Q_1Q_2 \cdots$ of the physical system in question. Since x is the ratio between the units of length in the two universes it can be any positive rational number, while the values for n_1n_2, etc., are either zero or whole numbers as given by our transformation equations. Under these conditions it is evident that we shall be able to obtain a *unique* solution for the form of F in equation (9) provided there are only two Q's (except for the particular case that n_1 and n_2 are zero). In case there are more than two Q's, equation (9) will not in general give a unique solution unless we have added information than that furnished by the principle of similitude; it will, however, often prescribe important limitations to the form of F.

We may now call particular attention to the fact that there is nothing to prevent the application of equation (9) to obtain relations which contain *dimensional constants* such as the R in the gas laws or the a in Stefan's law. We saw that the principle of dimensional homogeneity gave us no assistance in obtaining such relations because there is no way to know beforehand what the dimensions of these constants are going to be, and such knowledge is necessary in order to construct the dimensionless products which are the arguments of the desired functional relation (see equation 4). To use equation (9), however, no knowledge of these *dimensional constants* is necessary. They are quantities which in accordance with the principle of similitude must have the same magnitude in both universes U and U', and they do not occur among the measurements $Q_1, Q_2, Q_3, \cdots, Q_1', Q_2', Q_3', \cdots$ of those properties which have a different numerical magnitude depending on which observer measures them. The introduction of such dimensional constants in the final relation will occur because of the form of F and not because of its arguments.

A few simple examples of the application of the principle of similitude will make the foregoing analytical discussion clearer.

The Relation Between Mass and Energy.—The recent developments of physical science connected with the Einstein theory of relativity have led us to expect a relation between the mass m and energy U of any system. If there is such a relation between the mass and energy of a system, it is evident that the principle of dimensional homogeneity will provide us with no information as to the form of the relation since there is no dimensionless product possible of $[m]$ and $[ml^2t^{-2}]$, so that the relation must contain a dimensional constant whose dimensions must be determined by other considerations. The principle of similitude, however, will permit a solution of the problem. We may write

$$m = F(U) \tag{10}$$

where F is the unknown function whose form is to be determined. If, however, there is a general relation connecting the mass and energy of any system, measurements made by O' on the same system which satisfy (10) would have to lead to the equation

$$m' = F(U'), \tag{11}$$

where in order to agree with the principle of similitude F has the same form as above.

Substituting our transformation equations for mass and energy and combining with (10) we obtain

$$m = x\,F\left(\frac{U}{x}\right) = F(U),$$

and since x may be any number the only solution for this functional equation is

$$m = kU, \tag{12}$$

where k is some constant. We have thus derived the important principle, familiar in the newer mechanics, that the mass of a system is proportional to its energy.

In order to make equation (12) agree with the principle of dimensional homogeneity it is evident that we shall have to assign to k the dimensions of the reciprocal of velocity squared, and as a matter of fact the constant has turned out to be the reciprocal of the square of the velocity of light.

The Relation between the Energy Density of a Hohlraum and the Temperature.—The energy density in a hohlraum at thermodynamic equilibrium is a function of the absolute temperature T. There is, however, no dimensionless product of $[u] = [ml^{-1}t^{-2}]$ and $[T]$, so that we cannot determine the form of the functional relation connecting the two quantities from dimensional considerations. We have, however, from the principle of similitude the equations

$$u = F(T),$$

and

$$u' = F(T'),$$

which would both be true since our system would obviously appear to both observers as a hohlraum at thermodynamic equilibrium. Substituting the transformation equations for u' and T' and combining we have

$$u = F(T) = x^4 F\left(\frac{T}{x}\right),$$

for which the only solution is

$$u = aT^4 \tag{13}$$

where a is a constant. We have thus derived Stefan's law from the principle of similitude, and having determined the form of the relation we now see that the constant a must have the dimensions $[ml^{-1}t^{-2}T^{-4}]$ to agree with dimensional considerations.

The Gas Laws.—There is a general relation connecting the pressure p, temperature T, volume v, and number of mols N of a perfect gas; there is, however, no dimensionless product of the quantities p, v, N and T, so that the principle of dimensional homogeneity will give us no assistance in determining the form of the relation. Let us suppose, however, an ideal gas composed of rigid elastic particles: such a system would evidently appear to both observers to be composed of rigid elastic particles, and hence would follow the same general laws in both universes. We may write

$$F(p, v, N, T) = 0 \tag{14}$$

for the measurements of O, and

$$F(p', v', N', T') = 0 \tag{15}$$

for the measurements of O', where, to accord with the principle of similitude, F must have the same form in both equations. Since N, the number of mols of gas in the system under consideration, could be determined by counting the number of molecules present, its value will appear the same both to observer O and O', and for the other quantities we have the transformation equations in Table II. Substituting in equation (15) and combining with (14) we obtain

$$F(p, v, N, T) = F(p', v', N', T') = F\left(\frac{p}{x^4}, x^3v, N, \frac{T}{x}\right) = 0.$$

There is no unique solution for this equation. If, however, we assume Boyle's Law that the pressure volume product is a constant at a given temperature, and Avagadro's hypothesis which makes the pressure volume product proportional to the number of mols of gas, we may rewrite our equation in the form

$$F_1\left(\frac{pv}{N}, T\right) = F_1\left(\frac{p'v'}{N'}, T'\right) = F_1\left(\frac{pv}{xN}, \frac{T}{x}\right) = 0,$$

and the only solution of this equation is in the form

$$\frac{pv}{NT} = R, \quad pv = NRT,$$

where R is a constant. Given the principles of Boyle and Avogadro, we have thus derived the Law of Charles from the principle of similitude. To agree with dimensional considerations R must have the dimensions of heat capacity per mol.

Other applications of the principle of similitude will be found in the articles already referred to; see also an article by G. Nordström[1] for a discussion of the intimate relation between the principle of similitude and his theory of gravitation.

Limitations of the Principle of Similitude.—There are limitations to the application of the principle of similitude to some extent similar to those found in dimensional reasoning. In the first place, just as in the case of dimensional reasoning, we obtain from such considerations no information as to the magnitude of the constants which are introduced into our equations, while a derivation of the same relations from the considerations of the special field in question usually provides such information.

It should also be noticed that just as in dimensional reasoning we have to know or assume *just what are the quantities* which we shall expect to find connected by a physical equation. If we leave out some quantity which belongs in our relation, we shall deprive our functional equation of a necessary multiplier, of the form x^n, and shall thus obtain an incorrect result. Similar considerations would apply to the introduction of an unnecessary quantity.

We must also call attention to the fact that we must necessarily restrict our application of the principle of similitude to systems which could form equally well a part of universe U or universe U', and whose properties would be connected by the same functional relation in both universes. It is a little difficult to be quite sure as to the actual significance and scope of this restriction. It is perhaps identical with the fact that in order to apply the principle of similitude we must be sure to introduce all the physical quantities which are necessary to the complete physical equation.

Relation of the Principles of Dimensional Homogeneity and of Similitude.

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[1] Öfversigt af Finska Vetenskaps-Societens Förhandlingar, Bd. *58* (1914–15), Afd. A, No. 22.

—In conclusion it will now be possible to state the principles of dimensional homogeneity and of similitude in such a form as to make their relation and difference quite evident. As we have already seen the principle of dimensional homogeneity requires that all the essential equations of physics shall be unaltered if we substitute for every length in the equation a value x times as great, for every interval of time a value y times as great, for every mass a value z times as great, and so on for all the fundamental properties. For measurements of derived properties which enter the equation we must substitute their value multiplied by the appropriate combination of x, y, z, etc., which is obvious from their dimensions. It should be particularly noticed, however, that this invariance will not obtain in those equations which contain constants like the R of the gas laws or the a of Stefan's law, unless indeed we assign suitable dimensions to these constants.

In comparison with the above requirement, the principle of similitude requires that the equations to which it applies,[1] shall remain invariant when the various measurements are multiplied not by a combination of different multipliers x, y, z, etc., one for each fundamental property, but when they are multiplied by different powers of the one quantity x as given in the table of transformation equations. Moreover, the quantities which have to be so multiplied in order to obtain invariance include only those actually measured, and not any of the so-called dimensional constants.

These parallel statements will make the relation of the two principles evident. Where dimensional constants enter, the principle of dimensional homogeneity is of no avail in predicting the form of a relation, since we cannot tell beforehand what the dimensions of the constant are going to be. For such problems we must have recourse to the principle of similitude. On the other hand, when dimensional constants do not enter into the relation, although we may apply either principle, the principle of similitude is usually the less powerful since it merely prescribes invariance when the different measurements are multiplied by powers of a single arbitrary multiplier x, while the principle of dimensional homogeneity prescribes the more drastic requirement of invariance when the multiplications are carried out with a different arbitrary multiplier for each fundamental property.

As an example of the greater power of the principle of dimensional homogeneity in a case where both principles are applicable, we may consider again the relation between the velocity v of a compressional wave and the density ρ and elasticity E of the liquid. We have from our table of dimensions

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[1] *I. e.*, equations connecting the properties of systems capable of forming part either of U or U'.

$$[v] = [lt^{-1}],\ [\rho] = [ml^{-3}],\ [E] = [ml^{-1}t^{-2}],$$

and see that the only *independent* dimensional product is of the form $v^2(\rho/E)$ and hence that our relation must be of the form

$$v = k\sqrt{\frac{E}{\rho}}.$$

If we apply the principle of similitude to the same problem we obtain

$$v = F(\rho, E),$$
$$v' = F(\rho', E'),$$

or substituting our transformation equations and combining

$$v = F(\rho, E) = F\left(\frac{\rho}{x^4}, \frac{E}{x^4}\right),$$

which has no unique solution but prescribes

$$v = F_1\frac{E}{\rho},$$

as a necessary form of the final relation. We see that in this case the principle of similitude leads to a correct result but does not provide such explicit information as the principle of dimensional homogeneity.[1]

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[1] These considerations might indicate that in those cases where both can be applied it is usually better to use the principle of dimensional homogeneity than the principle of similitude. Nevertheless, even in such cases there is sometimes an advantage from the point of view of simplicity and fundamentality in employing the principle of similitude instead of dimensional reasoning. Thus there are a number of electrical problems, in particular problems concerning the properties of the electron, which were treated by the author in his first paper, *loc. cit.* Buckingham has shown (*loc. cit.*) that these same problems, although perhaps with less ease and directness, can be treated by dimensional methods. To do so, however, he has had to introduce the electric inductivity and magnetic permeability of the medium in which the electron in question is situated and take account of the dimensions of inductivity and permeability. From the point of view, however, of modern electromagnetic theory as developed by Lorentz, the inductivity and permeability of a medium is in the nature of a statistical result of the activities of individual electrons, and each actual electron is itself situated in *free space*. For this reason there are some advantages in treating such problems from the point of view of the principle of similitude.

UNIVERSITY OF CALIFORNIA,
February 11, 1915.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MECHANICAL STRAIN AND THERMOELECTRIC POWER.[1]

BY WALTER P. WHITE.

1. The emphasis generally and justly laid upon the importance of exact measurement has had one unfortunate consequence, in that phenomena, even though important, which do not lend themselves easily to measurement are apt to suffer a comparative neglect. Such is the case with some of the results of permanent mechanical strain in metals. It is difficult to specify definitely either the amount or character of the changes due to such strain; it is even uncertain what they consist in, and yet their effect upon the thermoelectric power may throw light upon the important and obscure questions which exist regarding the relations of electricity to metals. A few observations upon this effect are therefore given here.

2. In general, the effect of alloying a metal is to lower the thermoelectric power. The effect of hardening by permanent strain (bending, drawing through dies, etc.) either a pure metal or an alloy is to *raise* the power. Hence hardening has an opposite effect to alloying, though of less amount. Platinum alloys, however, are most of them higher than platinum. And the alloy of platinum containing 10 per cent. of rhodium (and probably other platinum alloys also) is lowered by mechanical hardening, so that here also alloying and hardening have effects opposite to each other. Pure platinum, however, is changed in the same direction by hardening and (usually) by alloying.

One probable result of this opposite behavior of pure platinum and its alloys is that there are alloys of such compositions that hardening has no effect on their thermoelectric power. And it is possible, also, that this result might be strictly true for one sort or method of hardening, but not for others, so that various methods would cause an alloy of the proper composition to vary in opposite ways. If this is so, it opens up a new line of investigation upon the character and effects of permanent strain.

The platinum metals, on account of their freedom from oxidation, and the consequent ease of annealing, are very well adapted for investigations of this character.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

3. The thermoelectric effects of temporary strain (strain below the elastic limit) have no perceptible relation to those due to permanent strain, or hardening. Hydrostatic pressure raises the thermoelectric power in metals and alloys, though with some exceptions, of which manganin is one. But I found that tension lowered the thermoelectric power for platinum, platinum-rhodium, copper, and constantan, and raised it for manganin. The magnitude of the effect was very roughly the same for copper as with pressure (6×10^{-6} microvolts per degree per kg./sq. cm. against 3×10^{-6} quoted by Baedeker for pressure), was more for platinum, less for manganin and constantan. It will be noticed that *temporary* strain affects platinum-rhodium like platinum and most other metals. Both platinum and its alloy showed nearly or quite an identical effect from tension when hard and when annealed, but the alloy gave less than half as much as platinum.

4. A certain sample of constantan wire, hardened by drawing from 2.5 to .25 mm. diameter, was softened by careful annealing near 800°. Another portion of the same, annealed near 300°, remained mechanically rather hard, but was as soft, *i. e.*, as low, thermoelectrically, as the other. *A metal, therefore, may be in a state of relative mechanical hardness without possessing the corresponding thermoelectric condition.* The same effect has been observed with platinum, which is generally annealed perfectly at a dull red heat, though not then so soft mechanically as after a heating to 1300° or so. In one instance, however, the thermoelectric power was lowered by a high heat after it had become apparently constant by heating to a dull red.

5. Even in a short and simple communication upon thermoelectricity, it seems necessary at the present time to specify what convention is used regarding the sign of the thermoelectric power. The best authorized notation, used from the discovery of thermoelectricity in 1821, and sanctioned by the leading texts and collections of tables in English, French, and German (with the exception of Mascart and Joubert) defines that metal as positive from which the current flows at the cold junction. This makes antimony, iron, copper, and platinum-rhodium positive to platinum, mercury, nickel, constantan, and bismuth.

The opposite notation has, however, been used in some cases, upon what grounds I have been unable to learn, but with the result of causing much confusion. Thus A. L. Bernoulli published in 1910 a theory of thermoelectricity[1] which, on account, as he explains, of this confusion of signs, gave results directly opposite to observation, and therefore had to be modified so as to reverse the sign of the results predicted—a feat which he promptly and successfully accomplished.[1] Even so, however, he still suffered from the confusion apparently, for he takes the platinum rhodium alloy to be negative towards platinum, and finds that this is in accord with his second theory, whereas this alloy is really positive. At about the same time Koenigsberger, who used the unauthorized system of signs, was thereby deceived into thinking that he had obtained the same value for silicon as Wick, whose signs were correct. Again, the last (1914) edition of the Smithsonian Tables gives thermoelectric power in different ways on different pages. This contradiction is soon to be corrected in a new issue.

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[1] Ann. Physik, 33, 690.

[2] Verh. d. Phys. Gesell., 1911, 213.

In this abstract the authorized convention as to sign has been followed.

NEW BOOKS.

Unit Photography. F. M. Steadman. New York: D. Van Nostrand Co., 1914. Pp. xi + 160. Price, $2.00.

The purpose of the book announced in the introduction is a desire to establish a rational scientific foundation for the practice of photography. The author proceeds first to demonstrate the fact that such a foundation is lacking at the present time. Those who have had practical experience in photography, even as amateurs, need very little persuasion or argument to convince them of the justification of this conclusion. The bewildering confusion of lens speed, diaphragm opening, sensitometer number, emulsion number, season of year, time of day, state of the weather, character of the subject and finally the all important question of length of exposure necessary to secure a satisfactory negative which confronts all beginners and the great majority of somewhat experienced workers is too well realized to require any special emphasis. The reviewer has dabbled in amateur photography from time to time for a period of nearly thirty-five years and has been constantly impressed by the utter lack of any real systematic progress in the scientific aspects of the subject. Although there has been an enormous increase in the manufacture and use of photographic apparatus, and although a great number of people have cameras of one sort or another and use them occasionally, the available rules for operating have retained their primitive simplicity and uncertainty. The one fundamental essential of satisfactory photographic work is the securing of a correct, initial exposure and the necessary requirements for obtaining this are the ones which have received the least systematic and intelligent consideration up to the present. In the opinion of the author, "a perfect exposure is one which creates in an emulsion a latent image which may be developed under known conditions and without special attention, into exactly the character of negative which the worker in that particular case desired to obtain."

The book is written with the object of providing a practical method for determining the proper exposure from a study of the light values of the subject, the size of the diaphragm opening and the speed of the emulsion. Discussing the question of the light values of the subject the author makes use of the expressions "actinism" and "actinity." The latter is defined as "the capability of radiation to produce certain chemical changes on converging at a point." The general bearing of these factors on the chemical action produced in the emulsion is discussed and explained. The importance of the solid angle subtended by a given object is emphasized as being one of the elements requiring consideration. The author describes a simple and apparently practical device which is to be used as an actinometer and a considerable number of practical problems in actinometry are stated and solved in illustrating the manner in which the apparatus is employed. The subjects subsequently treated include the comparison of different actinicities, the classification of the subjects to be photographed, the Hurter and Driffield system and the general topic of negative making. The important element of the latitude and endurance of emulsions and the bearing of these on the nature of the subject and the time of exposure are discussed in a very enlightening manner.

The reader of this book can not avoid being impressed by the sane and practical treatment which the subject has received in the hands of the author. The book contains a good deal of valuable information and affords intelligent answers to many of the questions which have long perplexed the average photographer. It is perhaps unfortunate that the plates, of which there are thirteen given, do not possess greater artistic merit, although from the standpoint of photographic technique they are in all respects satisfactory.

B. B. Boltwood.

Optic Projection. By S. H. Gage and H. P. Gage. Ithaca: Comstock Publishing Co., 1914. Price, $3.00.

While this manual is written especially from the standpoint of the user of projection apparatus and of the manufacturer, it is thorough and scientific, and the physicist will find in it a clear exposition of the principles involved. First the use of the magic lantern with different methods of illumination is taken up in detail, then micro-projection, and motion picture apparatus, concluding with the optics of projection and its application in physics and in the study of vision.

Detailed instructions and practical hints are given throughout. The book shows intimate knowledge of the most modern apparatus derived from close contact with the manufacturer, and this knowledge is presented clearly and compactly by the constant use of excellent plates and diagrams. An interesting historical sketch is given as an appendix, with a list of manufacturers, and a complete bibliography. Altogether the book deserves praise, and makes a valuable addition to the literature on projection.

P. V. W.

Second Series. *October, 1915* *Vol. VI., No. 4*

THE

PHYSICAL REVIEW.

MAGNETIZATION BY ROTATION.[1]

By S. J. Barnett.

§1. In 1909 it occurred to me, while thinking about the origin of terrestrial magnetism, that a substance which is magnetic (and therefore, according to the ideas of Langevin and others, constituted of atomic or molecular orbital systems with individual magnetic moments fixed in magnitude and differing in this from zero) must become magnetized by a sort of molecular gyroscopic action on receiving an angular velocity.

Thus consider a cylinder of iron, with zero magnetic moment in its initial state. If it is given an angular acceleration about its axis, each individual system, which we may suppose for simplicity to consist of a number of electrons revolving in fixed orbits with constant average velocities about an oppositely charged nucleus, will change its orientation in such a way as to contribute a minute angular momentum, and therefore a minute magnetic moment, parallel to the axis of the cylinder. This increment of angular momentum of each system is in the direction of the axis of rotation, and the corresponding increment of the magnetic moment is either in this direction or in the opposite direction according as the particles in revolution are positive or negative. If the revolving electrons are all negative, in conformity with most of the experimental evidence, the cylinder will become magnetized in the direction in which it would be magnetized by an electric current flowing around it in a direction opposite to that of the angular velocity imparted to it. This corresponds to the direction of magnetization of the earth and the sun.

§2. Preliminary experiments made at the Tulane University of Louisiana at the time this idea occurred to me appeared to show,[2] though doubtfully, a very minute effect of the sort in question, on the assumption that the revolving electrons are negative, in the case of a steel rod about

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[1] Revision of papers read before the Ohio Academy of Sciences, November, 1914, and the American Physical Society, November, 1913, December, 1914, and April, 1915.

[2] S. J. Barnett, Science, 30, 1909, p. 413.

7 cm. in diameter and half a meter long driven at a speed of about 90 revolutions per second. In these experiments two approximately cylindrical and similar electromagnets were mounted with their axes parallel and approximately perpendicular to the earth's intensity. One of the cores and both of the coils were fixed while the other core was rotated by an induction motor at a distance. The two coils were connected in series through a ballistic galvanometer in such a way as to compensate for any change of flux due to alteration of the earth's intensity. Changes of flux were determined by the galvanometer throws occurring on starting and stopping the motor. Later observations made in much the same way, but with an attempt at improvement in apparatus, failed to confirm this result with any certainty; and further investigation of the subject was postponed until better facilities were available.

§3. In 1912 a similar idea was advanced by Schuster[1] in his presidential address before the Physical Society of London. He also appears to have been led to his views by considering the origin of the earth's magnetism.

Referring to other hypotheses as to the production of magnetization by rotation, and assuming, for the sake of argument, that they account for terrestrial magnetism, he shows that one of the hypotheses cannot be correct, as it would then have been easily established by common observations on rotating bodies, and that the other leads to effects too minute to be detected by the most refined observations.

He then takes up the hypothesis similar to that introduced here,—a hypothesis according to which rotation, instead of *directly determining magnetization*, "determines magnetic intensity which may or may not cause magnetization according to the nature of the body." "It is," he says, " . . . quite in accordance with our present views that every rotating body should be subject to a magnetizing force along the axis of any rotation that may be impressed upon it. If magnetization be due to a circulation of electrons within the molecules these should to some extent behave like gyrostatic compasses, setting themselves parallel to the axis of rotation of the body which contains them. Further properties of molecular constitution have, however, to be specified before we can say whether any actual magnetization results. If the electron is free,[2] the main result, I believe, would be only a magnetic precession round the axis of rotation, and in this we may find a powerful argument [for this explanation of terrestrial magnetism], because the same cause which gives us the magnetic force, also gives us the secular variation[3] . . . "

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[1] A. Schuster, Proc. Phys. Soc. London, 24, 1911–12, p. 121.

[2] A hypothesis contrary to mine.

[3] In this address Schuster refers to an address made eleven years earlier in which he suggested the possibility "that terrestrial magnetism is due to the rotation of the electron round

"On the other hand, the theory [in order to account for terrestrial magnetism] would have to explain why the iron inside the earth becomes more strongly magnetized than the iron in our laboratories. There is, of course, always the possibility of some substance being subject to the effects of rotation in a much higher degree than iron. Such questions can only be settled by experiments which are now in progress." On the importance of these, and other such experiments, Schuster lays great stress.

§4. It soon occurred to me that the effect under investigation was the converse of the effect predicted and looked for by O. W. Richardson[1] in 1907–8, viz., the production of rotation by magnetization; and it became apparent that both effects were immediate consequences of an idea advanced long ago according to which a magnet must behave like a gyrostat if the Ampèreian currents consist in the motion of actual matter. This idea is due to Maxwell,[2] who constructed apparatus for experiments upon the subject as early as 1861.

In Maxwell's experiments an electromagnet was pivoted in a frame in such a way as to be free to rotate about a horizontal line through its center of mass and perpendicular to its magnetic axis. With the magnetic axis making an angle θ with the vertical, the frame was rotated at high speed about a vertical axis, and optical observations were made for a change in θ, stability having been secured by suitable adjustments of the principal moments of inertia. No change was detected, but only rough observations were possible.

My own experiment may be considered as a modification of Maxwell's, and the principal equation in the development of its theory, after that giving the relation between the angular momentum and the magnetic moment of a molecular magnet, is a special case of his equation for the torque acting to diminish the angle θ. In my experiment Maxwell's electromagnet is replaced by each of the countless multitude of molecular magnets of which the iron rod is constituted, and the total change in the orientation of all these magnets with reference to the axis of rotation of the rod is determined magnetically instead of optically.

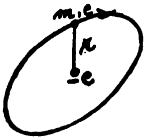

Fig. 1.

§5. A quantitative theory of the effect will now be developed.

Consider the simplest type of molecular magnet (Fig. 1), in which a single particle with charge e and mass m revolves in a closed orbit about

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the atom" as a means of explaining magnetic precession. The quotation from this earlier address, of which I first learned from the 1912 paper, would indicate that Schuster had probably in mind in 1901 the idea which he proposed definitely in 1912.

[1] O. W. Richardson, Phys. Rev., 26, 1908, p. 248.

[2] Electricity and Magnetism, § 575.

a much more massive nucleus with charge $-e$. If r denotes the radius vector, ω the angular velocity, $\alpha = \frac{1}{2}r\omega^2$ the areal velocity, μ the magnetic moment of the molecular system, and M the angular momentum due to the orbital motion, we have

$$\mu = e\alpha \quad \text{and} \quad M = mr^2\omega = 2m\alpha. \tag{1}$$

Hence

$$\frac{M}{\mu} = 2\frac{m}{e}, \quad \text{or} \quad M = 2\frac{m}{e}\mu; \tag{2}$$

so that the angular momentum is directly proportional to the magnetic moment.

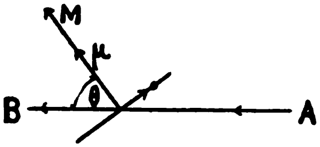

Fig. 2.

If the normal to the orbit (Fig. 2) makes an angle θ with any direction AB, the component of the magnetic moment μ in this direction is $\mu \cos \theta$, and that of the angular momentum is thus

$$M \cos \theta = 2\frac{m}{e}\mu \cos \theta.^1 \tag{3}$$

If the body of which the molecular system of Figs. 1 and 2 is a part is set into rotation about the axis AB with angular velocity Ω, the angle between the vector representing M, the angular momentum of the system due to its orbital motion, and AB will decrease, just as in the case of a gyroscope, until the torque T' on the revolving system brought into existence by this displacement is just equal to the rate of increase of its total angular momentum in the steady state when kinetic equilibrium has been attained and the vector M is tracing out a conical surface with constant semiangle θ and angular velocity Ω. The effect in this steady

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[1] Assuming m/e identical for all the orbital systems, and summing over the unit volume, we have

$$\Sigma M \cos \theta = 2\frac{m}{e}\Sigma\mu \cos \theta = 2\frac{m}{e}I, \tag{4}$$

which is the formula developed by Richardson (l. c.), but by a complicated process. Here $I = \Sigma\mu \cos \theta$ is the intensity of magnetization, and $\Sigma M \cos \theta$ is the angular momentum of the electrons per unit volume, both reckoned in the direction AB.

This fundamental equation of Richardson's theory is developed in essentially this same manner, in which it was presented in the first two papers which this article reports, in a more recent paper presented by Einstein and de Haas in February and April (D. Ph. Ges., No. 8, April 30, 1915). In this paper are described experiments on soft iron by the method of resonance which appear to confirm Richardson's theory. I had myself started experiments on this effect, beginning with the ballistic method but planning to use the method of resonance if necessary. From my ballistic experiments I can state that in the case of brass no effect exists comparable with that which the simple theory indicates should exist in the case of iron. Einstein and de Haas have found the same thing true of copper. Their paper contains no reference to the previous work of Maxwell, Schuster, Richardson, or myself.

state is exactly the same as if the body were at rest and the system were acted upon by a torque $T'' = -T'$ due to an extraneous magnetic field with strength H equal to the intrinsic magnetic intensity of rotation. The complete expression for T'' is known (and can readily be shown from first principles) to be

$$T'' = -T' = -M\Omega \sin\theta - B\Omega^2 \sin\theta\cos\theta, \tag{5}$$

where B denotes the excess of the moment of inertia of the system about the axis of its orbital angular velocity ω over the moment of inertia about that diameter of the orbit making with AB the angle $90° - \theta$. If the orbit is circular

$$B = mr^2 - \tfrac{1}{2}mr^2 = \frac{M}{2\omega}. \tag{6}$$

Eliminating B and M from (5), we get

$$T'' = -\mu \sin\theta \cdot 2\frac{m}{e}\Omega\left(1 + \tfrac{1}{2}\frac{\Omega}{\omega}\cos\theta\right).^{1} \tag{7}$$

Dividing this expression by $-\mu\sin\theta$, as in the case of an ordinary magnetic field, we get the intrinsic intensity of rotation:

$$H = 2\frac{m}{e}\Omega\left(1 + \tfrac{1}{2}\frac{\Omega}{\omega}\cos\theta\right).^{2} \tag{8}$$

The values of Ω experimentally attainable are so small in comparison with ω that the second term is negligible. If the orbit is not circular we obtain for H an expression whose first term is identical with that of (8) and whose second term has the same order of magnitude as that of (8).

If we assume that e/m has the value ordinarily accepted for the negative electron in slow motion, viz., -1.77×10^7, and put $\Omega = 2\pi n$, where n is the angular velocity in revolutions per second, we obtain for the intensity per unit angular velocity

$$H/n = -7.1 \times 10^{-7}\frac{\text{gauss}}{\text{r.p.s.}}. \tag{9}$$

This is on the assumption that the negative electron alone is effective. According to this, all substances would be acted upon by precisely the same intensity for the same angular velocity.

If some or all of the positive ions also have orbital motions, proportionality with angular velocity will evidently still exist, but the coefficient of Ω will be reduced in magnitude or even changed in sign, and the intensities acting on different substances may differ for the same value of Ω.

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[1] This equation, as stated above, also follows immediately from Maxwell's equation for the torque when the conditions here assumed are put in.

[2] The first term of this equation has been given previously by Einstein and de Haas (l. c.), but is incorrectly derived in their paper, equations for a *molar* magnet instead of a *molecular* magnet being employed. All the terms of their equations reduce to zero unless the body is originally magnetized.

If the influence of the negative electrons is preponderant, the number in (9) gives the ***maximum*** magnitude of H/n, attained when the negative electrons alone are effective.

The relation of proportionality must hold also between the angular velocity and the magnetic flux density and intensity of magnetization, which are very minute and therefore proportional to the intrinsic intensity; but these quantities will depend not only upon the intensity but also upon the material and shape of the rotating body. Thus in the case of a diamagnetic substance each of the orbits in an atom or molecule tends to change its orientation precisely as an orbit in a magnetic molecule; but no gross magnetic effect can, on the theory advanced here, result, because the geometric sum of the individual magnetic moments of the particle is permanently zero.

§6. In the experiments performed here two modifications of the earlier method have been tried, in both of which the galvanometer was replaced by a fluxmeter. In one series of experiments the magnetic circuit was constituted almost wholly of iron. The iron cylinder under investigation rotated between the pole-faces of a large U-shaped electromagnet, with minute air gaps; and the similar coils on the two legs of the iron core, connected in series in the usual manner, were put in the series with the fluxmeter. This apparatus was very sensitive, but the large extraneous reactions were such as to mask or make impossible of interpretation such minute effects as were under investigation.

§7. The other series of experiments, which has given definite and conclusive results, will be described in considerable detail on account of the newness of the effect obtained.

In these experiments two nearly similar rods of steel[1] shafting A and B (Fig. 3) were mounted with their axes horizontal and approximately at right angles to the magnetic meridian, and two similar coils of insulated wire were mounted about their centers. These coils were connected in series with one another and with a fluxmeter, and were oppositely wound like the coils of an ordinary U-shaped electromagnet, so that any variations in the intensity of the earth's field, acting in the same way on both rods, might produce no effect on the fluxmeter. One of the rods, which will be called the compensator, as A, remained at rest, while the other, called the rotor, as B, was alternately rotated and brought to rest, the change of flux being determined by the fluxmeter.

The approximate dimensions of the rods A and B as they were used in nearly all of the work, are indicated in Fig. 3. The dimensions of the two coils used in most of the work are also indicated in the figure. Each of these coils was wound on a brass bobbin with about 5,000 turns of No. 14 D.C.C. copper wire, the winding being made very regular on account of other investigations for which they were primarily designed.[1] A third coil, of somewhat different construction, was substituted for one of the coils in some of the experiments (see below, §23).

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[1] Steel, even when soft, has the advantage of freedom, or approximate freedom, from magnetic lag in weak fields, as shown long ago by Ewing (Roy. Soc. Proc., June 20, 1889), and confirmed by experiments on the steel rods used in this work.

§8. In the first part of the work the rotor was mounted in brass bearing pieces inserted in bronze castings bolted to the cement floor of the laboratory, all parts being accurately fitted so that there was as little play as practicable. The rotor was driven by a brass rod 1.4 meters long and 1.1 cm. in diameter, itself direct-connected to a counter-shaft and pulley system driven by belt from an alternating current motor of the repulsion type.[2] The countershaft and pulley system was entirely of brass, bronze, and wood, and moved in brass castings bolted to the floor, with thin iron sleeves for bearing pieces. The motor's pulley was similar to that of the countershaft, except that it was mounted on an iron sleeve. Excessive vibration of the connecting rod was prevented by three properly spaced pieces of wood fastened to the floor and pierced by holes of suitable diameter for the passage of the rod. This method of driving, together with frequent oiling and the slow starting of the motor by the insertion of a choke-coil in series with its field coils, eliminated almost completely magnetic changes in the rotor due to vibration. The compensator and rotor were mounted 2.8 meters apart in positions symmetrical with respect to the motor.

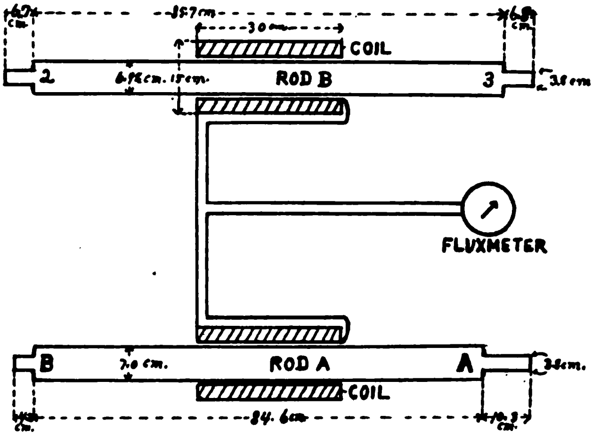

Fig. 3.

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[1] S. J. Barnett, "On electromagnetic induction and relative motion," Phys. Rev., 35, 1912, p. 323; "Some experiments on the magnetic field of two electromagnets in rotation," Phil. Mag., 26, 1913, p. 987; (London) Electrician, 74, 1914, p. 21.

[2] For the loan of this motor I am indebted to the department of electrical engineering.

§9. The fluxmeter was a Grassot instrument provided with a concave mirror with approximately 2 m. radius of curvature. It was mounted on a slate shelf cemented into the laboratory wall, and readings, with lamp and scale, were obtained to 0.1 mm. at a scale distance of approximately 2 m. Later on the scale distance was increased, usually to 8 m., a concave lens being added,[1] and all deflections have been reduced to this distance.

On account of the residual torsion of the suspension and the thermal electromotive forces in the circuit, the fluxmeter image usually drifts across the scale with greater or less rapidity, and it is necessary to compensate the drift by introducing suitable electromotive forces into the circuit. This was done by means of a potentiometer arrangement such as that commonly used in experiments on the Hall effect. As a result the drift was largely compensated, but ordinarily by no means as well as in the later experiments.

§10. In order to eliminate residual drift and other extraneous disturbances, readings were ordinarily taken in sets of eight, as follows: two with counter-clockwise or *negative* rotation (as seen from the west end of the rotor) four with clockwise or *positive* rotation, and two more with counter-clockwise or negative rotation, the order of the positive and negative rotations being sometimes reversed. The fluxmeter scale was read when the speed became steady, and again when the speed became so small that a minute quaver of the image became just visible, very slow rotation always producing a synchronous small vibration of the image. Mean deflections for the two directions were then obtained; and half the difference gave the change of flux produced by changing the speed from its maximum (which was the same in both directions) to a few revolutions per second.

To make the rotor run as smoothly as possible and to keep the bearings as free from deterioration as possible, the bearings were almost invariably oiled before taking each observation. Observations were made as the motor came to rest, instead of being made as it was brought to full speed, because the disturbances, both mechanical and electrical, were less for this procedure.

§11. The fluxmeter was standardized for changes of flux by introducing into its circuit, connected as in the rotation experiments, one coil of a low resistance mutual inductance standard, and making and breaking a circuit containing the other coil traversed by a current measured with a standard ammeter. To a precision of about one per cent. the fluxmeter gave 1 mm. deflection for 90 maxwells at the scale distance 8 meters.

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[1] The equivalent radius of curvature of this optical system depended greatly on the temperature, varying within the course of the work by more than 2 m. The optical system was otherwise poor, but the readings could be obtained with precision by making use of the narrow diffraction pattern produced with a carbon lamp glowing at extra voltage, or one of the new nitrogen filled tungsten galvanometer lamps made by the General Electric Company. For the opportunity of using one of these excellent lamps before they were placed on the market I am indebted to Mr. L. T. Robinson of this company.

Drift being eliminated, special experiments showed that the fluxmeter deflections for minute flux changes of the order of those occurring in the rotation experiments recorded here were independent of the time in which the changes occurred—as they are well known to be for large flux changes.

§12. To determine H_0, the intrinsic magnetic intensity of rotation per mm. of fluxmeter deflection at the scale distance 8 meters, the procedure was as follows:

Two equal wooden cylinders turned to the same diameter as that of rotor *B* were fastened coaxially to its ends, and the complete cylinder thus formed was wound (in three parts) on a lathe with a nearly uniform solenoid of insulated wire, 8 turns to the inch. The complete solenoid was about three times as long as the rotor occupying the central part. The solenoid was connected in series through a key with a constant battery of electromotive force 2.02 volts and an adjustable standard resistance box. With a resistance of 5,000 ohms in the battery circuit, and the fluxmeter circuit arranged as in the rotation experiments, the fluxmeter deflection was obtained repeatedly when the battery circuit was reversed in both directions. Many previous experiments had proved that with such minute magnetomotive forces or currents as were involved in these experiments and the other calibrating experiments described below, fluxmeter deflections, as would be expected, were strictly proportional to currents.

If h_0 denotes the solenoid's magnetic intensity per mm. deflection at 8 m., and *D* the mean fluxmeter deflection at 8.5 m., the scale distance at which these observations were made, we have from what precedes and the well-known formula for the magnetic intensity within a long uniform solenoid

$$h_0 = \frac{\frac{4\pi}{10} \times \frac{8}{2.54} \times \frac{2.02}{5{,}000}}{\frac{8.0}{8.5} \times \frac{D}{2}} \frac{\text{gauss}}{\text{mm.}} \tag{10}$$

The experiments were made with two different distances between rotor and compensator, viz., 1.2 m. and 1.6 m. The values of *D* for the two sets did not differ by as much as one third per cent. The mean value of *D* was found to be 273 mm., at the scale distance 8.5 m.

The long solenoid was desirable in order to obtain as nearly uniform a calibrating intensity as practicable, the intrinsic intensity of rotation being strictly uniform throughout the rotor. On account of the fact that the calibrating intensity acts on both the iron and the aether which permeates it, while the intrinsic intensity of rotation acts upon the iron only, it was desirable to eliminate the effect of the solenoid alone by making a separate experiment with no iron in the solenoid. Experiments of this kind showed that the deflection produced by the solenoid alone was 1.6 per cent. of that produced by the solenoid and core.

From this fact and equation (10) we get for H_0

$$H_0 = h_0(1 + 0.016) = 1.26 \times 10^{-5}\frac{\text{gauss}}{\text{mm.}} \qquad (11)^1$$

Approximate calibrations were also made with a similar solenoid wound on the rotor alone,[2] with distances 2.8 m., 1/3 m. and 1/4 m., between rotor and compensator. These gave for H_0, in the unit used above, 1.25×10^{-5}, 1.14×10^{-5}, and 1.07×10^{-5}, respectively.

§13. To determine B_0 and I_0, the flux density and intensity of magnetization per mm. deflection at 8 m. produced by the rotation H_0, a second experiment was necessary. A coil of 200 turns of insulated copper wire was wound over the central 10 cm. of the long solenoid and connected in circuit with the fluxmeter, the total resistance of the fluxmeter circuit being made equal to its former value by the addition of extra resistance from a box. The mean fluxmeter deflection was then obtained on reversal of a solenoid current just four times as great (1,250 ohms being now in the solenoid circuit) as that used in the first experiment. For the rotor-compensator distances 1.2 m. and 1.6 m. the same deflection (within 1/7 per cent.), 70.6 mm., was obtained at the scale distance 8.5 m.

The cross-section of rotor B was 37.8 cm.^{2}, and the fluxmeter constant was, as stated in §11, 90 maxwells per mm. at 8 m. Hence if δB denotes the change of flux-density in the first experiment, and $\Delta B = 4\delta B$, therefore, that in the second, we have for the actual change of core flux in the second experiment

$$\Delta B \times 37.8 \text{ cm.}^2 = \frac{70.6}{200} \times \frac{8.0}{8.5} \times 90 \text{ maxwells.}$$

The same change of core flux with the first arrangement of coils would have produced at the scale distance 8 m. the deflection $4 \times 273 \times 8.0/8.5$ mm. Hence, as this was the arrangement used in the rotation experiments, we have for the flux-density produced by rotation per mm. deflection at the scale distance 8 mm.,

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[1] Calibrations made before and after the principal experiments, and with methods and standardized instruments varied, were all in close agreement.

[2] Elimination of the extra length of solenoid almost exactly compensated for the small effect produced by the solenoid with iron removed.

$$B_0 = \frac{1}{37.8} \times \frac{70.6}{200} \times \frac{1}{4 \times 273} \times 90 \left(\frac{\text{maxwells}}{\text{cm.}^2}\right) \text{ per mm.} \tag{12}$$

$$= 7.7 \times 10^{-4} \left(\frac{\text{maxwells}}{\text{cm.}^2}\right) \text{ per mm.}$$

In connection with the approximate determinations of H_0 at the rotor-compensator distances 2.8 m., 1/3 m., and 1/4 m., mentioned in the last section, determinations of B_0 were also made giving the values 8.1×10^{-4}, 7.3×10^{-4}, and $6.9 \times 10^{-4} \left(\frac{\text{maxwells}}{\text{cm.}^2}\right)$ per mm., respectively.

The intensity of magnetization at the central section of the rotor per mm. deflection, which will be denoted by I_0, is approximately

$$I_0 = B_0/4\pi. \tag{13}$$

§14. With the apparatus now described over twenty-five sets of observations were obtained. The rotations of one group were made with rotor *A*, most of them at about 50 r.p.s., two at about 18 r.p.s. Those of the other group were made with rotor *B*, some of them with the end designated as "end 2" east, the remainder with the rotor reversed, all at about 50 r.p.s.

Each of the groups gave a mean result (differential deflection) in the direction predicted by theory on the assumption that the revolving electrons are negative, the mean deflection (reduced to 8 m. scale distance) per unit speed being about 0.04 mm.; but the discrepancies were large, partly on account of imperfect compensation of the earth's intensity owing to the large distance between rotor and compensator, partly on account of non-uniformity and imperfect compensation of fluxmeter drift, and partly on account of mechanical vibration and other causes.

§15. As had proved to be the case in the Louisiana experiments, there was always superposed on the deflection which apparently corresponded to the effect under investigation a deflection independent of the direction of rotation. Moreover, in one set of observations made on rotor *A* to see whether either effect was altered by reversing the residual magnetism of the rotor, it was found (and the same thing had been found in the earlier experiments), that no alteration occurred (see further, §34). But reversing the ends of a rotor invariably reversed the absolute deflection.

§16. In seeking an explanation of these phenomena and a justification of the method of investigation a number of experiments were made. In the first place it had been assumed that an alternating flux through the fluxmeter circuit would not affect the scale reading provided the frequency exceeded a few cycles per second. An alternating flux was always produced by the rotation of the rotor on account of lack of symmetry of its residual magnetization with reference to the coil, and by the stray flux from the alternating current motor.

To investigate this matter, one coil of a low resistance mutual inductance standard was placed in the fluxmeter circuit and the effect on the reading noticed when the other coil was traversed by an alternating current of such magnitude as to produce changes of flux through the other coil and fluxmeter of the same amount as occurred during the slow rotation of the rotor. Absolutely no effect was produced by making or breaking the alternator's circuit, the frequency being 40 cycles per second. Even changes of ten and one hundred times this amount, at frequencies of about 33 and 63 cycles per second, respectively, produced either no effect or (in the case of the latter) sometimes a slight effect on breaking the circuit. Neither was any change produced by driving the alternator from rest up to full speed, the circuits being permanently closed.

A related test was made with the motor itself. The motor, on being started, usually produced a quick throw of a number of mm., sometimes in one direction, sometimes in the other. This irregular effect quickly disappeared and did not reappear on stopping the motor. To test the effect of the motor on the permanent deflection, the fluxmeter was disconnected from the rotor and compensator coils and connected to another short thick coil provided with an iron core and placed near the motor. With this arrangement, and the motor driving the rotor as before to insure the expenditure of the same power as in the principal experiments, irregular throws, similar to those which occurred in these experiments, were produced on starting the motor, but the change of reading on the motor's coming to rest was either very slight or zero.

Further experiments on the fluxmeter are described below.

Suspicion that the effects might be due to a very slight longitudinal displacement of the rotor, or a very slight angular displacement of its axis, was easily shown by experiments to be groundless. All possibility of electric disturbances, which gave considerable trouble in a part of the work referred to in §6, was eliminated by earthing the fluxmeter circuit.

§17. It seemed possible that the second effect mentioned in §15, also the curious difference between the effects of reversing the rod and reversing the magnetization, and perhaps also with them even the first effect could be explained as consequences of the induction of electric currents in the rotor by its rotation in the earth's magnetic field. An effect of such currents upon the rotor coil must ordinarily exist even though it is wound with the turns almost precisely perpendicular to the rotor.

The change in sign of the mean deflection on reversal of the rotor pointed toward inhomogeneity; and it seemed possible to account for the identity of sign of the deflections for both directions of rotation by the shift of the stream lines of the induced currents with the reversal of this direction.

Figs. 4 and 5 illustrate an extreme case, in which, on account of symmetry, the fluxmeter deflection would be the *same*, in both direction and magnitude, for both directions of rotation of the rotor, *A*. In the first figure the stream-lines, the cross-section of the symmetrical one of which is indicated by the black dots, are displaced anti-clockwise, in the second clockwise, with reference to the earth's intensity, with the result that the change of flux through the test coil *C* is the same in both cases. It is easy to arrange a test coil near the rotor in such a way as to obtain almost any relation between the deflections for the two directions of rotation.

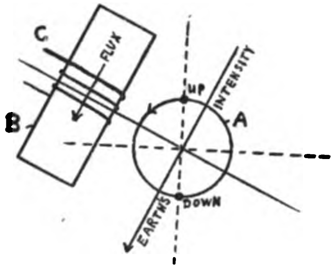

Fig. 4.

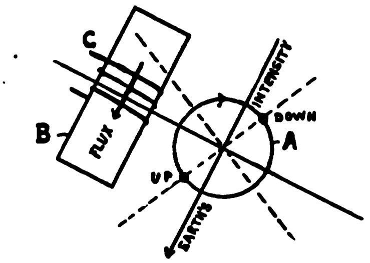

Fig. 5.

§18. An attempt was made to test this idea by altering as much as practicable the angle between the axis of the rotor coil and the axis of the rotor, although the free space between the rotor and bobbin was so small that only a small angular shift was possible. In the one complete and careful set of observations made, the mean deflections were altered considerably by the shift, but the sign of the deflections and the sign and magnitude of the differential deflections were not altered. In other, and rougher, experiments with different directions of the coil's axis, with one uncertain exception, no change of sign resulted. Moreover, later experiments, in which an irregularly wound coil was used, gave deflections in the same direction.

In another experiment the rotor coil was removed and mounted on a second compensating rod parallel to the first, the two being placed near and on opposite sides of the rotor. Rotating the rotor always produced a decided fluxmeter deflection.

§19. To get rid of the effects of induced currents in the rotor two methods were tried. First a rotor was constructed almost entirely of thin discs of iron, but its rigidity was insufficient. Resort was therefore had to the second alternative, viz., the compensation of the earth's intensity in the region occupied by the rotór by means of a large coil or cage of wire traversed by an electric current.

The framework of this cage was accurately constructed of brass and paraffined wood. The coil was about 1.5 m. in length (horizontal and approximately parallel to the rotor), $\frac{1}{4}$ m. in width (approximately normal to the earth's intensity), and $\frac{1}{7}$ m. in depth (approximately parallel to the earth's intensity). It was carefully wound of copper wire, uniformly except at the ends, where provision was made for the admission of the driving rod and rotor, and was mounted on the floor with its center approximately at the center of the rotor. A coil of these dimensions cannot, of course, produce a strictly uniform field in the region occupied by the rotor, and a much larger coil would have been made except for the expense involved in its construction and in properly mounting the rotating apparatus at a considerable height above the floor. Nevertheless it was capable of giving important information, and with it the first conclusive results were obtained.

§20. A few sets of observations on rotor *B*, with both end *2* and end *3* east, taken with the earth's field approximately annulled in this manner, gave results practically the same as those already described.

§21. In spite of the tests already described, suspicion still attached to the electric motor; and for a greater degree of certainty it was now replaced by a small air turbine made by adding to the countershaft and wooden pulley already described six uniformly spaced radial brass vanes. Compressed air was admitted to the vanes from four brass nozzles, two, symmetrically placed about the axis of the turbine, being open for each direction of rotation. The bronze shaft of the turbine was directly connected to the rotor by a brass rod 1.1 cm. in diameter and 0.3 m. long. For the final experiments the length was somewhat increased.[1]

Uncertainty as to the steadiness of the air pressure and speed made it necessary to add an instantaneous speed counter. For this purpose a very small separately excited dynamo, with a voltmeter across the armature terminals, was used. The dynamo was driven by a 24 ft. belt running on a pulley on the shaft of the turbine and the combination was properly calibrated, speeds in revolutions per second being obtained by multiplying the voltmeter reading by 0.566.[1] The speeds were sufficiently near to uniformity, the means for the clockwise and counter-clockwise rotations in a set not differing usually by as much as one r.p.s., and the individual speeds often differing by much less than this.

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[1] The rotation of the bronze countershaft, turbine wheel, and connecting mechanism, while the rotor was clamped, produced no effect on the fluxmeter although the speed was greater than the maximum speed of the rotor in the principal experiments.

§22. The observations with this apparatus were made in much the same manner as those already described, except that the fluxmeter reading for zero speed was obtained for a definite position angle of the rotor, instead of the reading for low speed. The turbine wheel was numbered at equal intervals around the periphery, and the zero reading was taken with a chosen one of these numbers uppermost, always the same throughout a set. The absolute deflection depends upon the number chosen, but the differential deflection does not, as was early found by direct experiment. This will be explained in §30.

§23. In this manner a number of sets of observations were obtained with both rotors and under various circumstances. These observations are given in Table I. For some of them the distance between rotor and compensator was made as small as ¼ or ⅓ meter, in order to compensate more readily the variations of the earth's intensity; but at such small distances apart the inductive action between the two rods is sufficient to modify the mean deflection greatly as is evident from the effect of reversing the compensator; though the effect on the differential deflection is very much less. In the last column but one, E signifies that the rotor was in the uncompensated field of the earth; $2E$ that the earth's field was approximately doubled in intensity by means of a current in the compensating coil; $-E$ that the earth's intensity was approximately reversed by a compensating current, and O that the earth's intensity was approximately compensated by the current in the cage.

It is to be remarked that in the case of every group (and the same is true of every set), however different the circumstances, the differential deflection has the same sign, and the positive sign, which, for the given arrangement of apparatus, means an effect in the direction predicted by theory on the assumption that the revolving electrons are negative.

Sets 13–18 were obtained with a rotor coil different from the two already described. It contained the same amount of the same kind of wire and had approximately the same dimensions and same constant in the fluxmeter circuit, but was not wound so regularly; and it was wound on a bobbin made of wood and fiber. This substitution was made in order to annul any possible effect of induced currents in the bobbin due to the lack of symmetry of the rotor's magnetization about

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[1] After all the rotations in this investigation were completed this calibration was checked and found to have remained unaltered.

TABLE I.

Deflections and Speeds.

Earlier Observations and Results.

Number of Group.	Number of Sets.	Rotor Used.	End East.	Distance Between Rotor and Compensator.	Mean Speed.	Mean Deflection for Negative Rotation (−).	Mean Deflection for Positive Rotation (+).	Differential Deflection (−) − (+).	Intensity of Field.	Remarks.
				m.	r.p.s.	mm.	mm.	mm.		
1	5	*B*	2	½	42	+ 9.3	+ 7.1	$+2.2(1.9)^1 \pm 0.9$	0	
2	4	*B*	3	½	45	+ 3.0	− 1.4	$+4.4(3.7)^1 \pm 1.1$	0	
3	2	*A*	*B*	⅓	42	−11.0	−13.1	$+2.1(1.9)^1 \pm 0.2$	0	
4	2	*B*	2	⅓	23	− 0.6	− 1.7	$+1.1(1.0)^1 \pm 0.1$	0	Compensator reversed in Group 5. { Mean reduced diff. defl. = +0.95 Mean speed = 26⅓
5	1	*B*	2	⅓	30	+ 2.5	+ 1.5	$+1.0(0.9)^1$	0	
6	1	*B*	3	½	47	− 1.3	− 4.4	$+3.1(2.6)^1$	2*E*	
7	1	*B*	3	½	45	− 0.5	− 4.9	$+4.4(3.7)^1$	*E*	
8	1	*B*	3	½	45	+ 4.6	+ 3.1	$+1.5(1.3)^1$	− *E*	
9	1	*B*	2	½	45	+15.4	+10.5	$+4.9(4.2)^1$	*E*	
10	1	*B*	2	½	45	+11.6	+ 8.8	$+2.8(2.4)^1$	− *E*	
11	1	*B*	2	1	42	+ 4.4	+ 1.8	+2.6	0	End *B* of compensator east.
12	1	*B*	2	1	39	+ 5.1	+ 2.8	+2.3	0	End *A* of compensator east.
13	1	*B*	2	1	45	+ 4.9	+ 1.0	+3.9	*E*	Rotor coil on insulating bobbin.
14	2	*B*	2	1	46	+ 7.0	+ 4.3	+2.6±0.5	0	Rotor coil on insulating bobbin.
15	2	*B*	2	1	32	+ 3.6	+ 1.9	+1.8±0.5	0	Same, also rotor in wooden bearings.
16	1	*B*	2	1	33	+ 4.0	+ 1.8	+2.2	0	Same, also cage circuits broken.
17	2	*B*	2	1	39	+ 5.9	+ 3.3	+2.6±0.2	0	Same, also iron bolts removed.
18	1	*B*	2	1	40	+ 8.0	+ 3.2	+4.8	*E*	" " " " "

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[1] The quantities in parentheses are the deflections reduced to the sensibility for the case in which rotor and compensator were 1 meter or more apart.

its axis. For a similar reason wooden bearings were then substituted for the metal bearings, and the brass circuits of the cage were cut. It was finally discovered that four small iron bolts had been accidentally left embedded in the cement floor, two near each end of the rotor (whose axis was about 13 cm. from the floor). These were removed. Observations made after each of these changes showed that they were without effect.

§24. The relation between the differential deflection and the speed was plotted on cross-section paper for groups 4–5, 11–12, and 14–17. As the table shows, 11–12, and 14–17 are the only groups for which the earth's intensity was annulled and the rotor-compensator distance as great as 1 m.; and groups 4–5 are the only ones with smaller distance and with earth's field annulled and compensator in both positions. Within the limits of the experimental error the deflection was proportional to speed. The mean of 4 and 5 was taken in order to eliminate as far as was possible the effect of the compensator. A straight line was drawn from the origin with slope obtained by dividing the sum of all the differential deflections by the sum of all the speeds, each group being counted as many times as it contained sets, except in the case of 4–5, which was considered equivalent to only 2 sets. The slope of this line was the weighted mean differential deflection per unit speed and equals 0.057 mm. per revolution per second.

§25. After the completion of the work thus far described it was decided to repeat the rotations in a region in which the earth's intensity was still more completely annulled.[1]

For this purpose it was necessary to mount the rotor and turbine about half a meter above the floor, and suitable piers were constructed of concrete. The two piers which supported the rotor were necessarily narrow (though much longer than broad) and inclined to the horizontal at about the angle of dip, and were therefore reinforced with brass rods cemented with them into the floor. The iron bearing sleeves of the turbine were replaced by vulcanized fiber, the iron pipe carrying compressed air to the turbine tubes was replaced by brass, and the earth's magnetic field in the region to be occupied by the rotor was carefully examined. In passing from one end of the rotor to the other the declination varied by about one degree, and the dip was uniform to at least one tenth degree. The rotor was mounted with its axis horizontal and perpendicular to the mean meridian. The original brass bearings in bronze castings were used, as they had been shown to be without injurious effect. The box to hold the compensating coil was rectangular in cross-section and about ¼ meter wide, like that used before, but was about 2 meters long and 1 meter deep. The framework was strongly and accurately built, chiefly of 2 in. × 4 in. and 2 in. × 2 in. well seasoned yellow pine. Over the two larger sides of this frame were screwed, in small sections, accurately planed boards of well seasoned white pine provided with accurately cut parallel and equally spaced uniform grooves to hold the wire. Boards of the same kind, except that they were not grooved, completed the wooden surface over which the coil was wound. All materials were non-magnetic, and all the woodwork was coated with paraffine to prevent warping. The coil was wound with 151 turns of No. 20 copper wire, each turn being all in one plane, except for the short end portions, which went over the ungrooved surfaces and were somewhat irregular. The passage from one turn to the next was made by a sharp turn at one corner of the frame, and the return wire was carried close to this corner. The wires were fastened to the bottoms of the grooves and held in place by paraffine. The width of the box was about 26.8 cm. (26.9 at the middle, 26.7 at the ends), the length about 197.9 cm., and the coil was 95.9 cm. long.

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[1] The desirability of this course was realized from the first and was also mentioned by Dr. Rosa at the Philadelphia meeting of the Physical Society, Dec., 1914.

§26. To test the degree of uniformity of the part of the magnetic field produced by the electric current in this coil in the region to be occupied by the rotor, the procedure was as follows: A test coil about 6 cm. long and 6 cm. in diameter, connected in circuit with the fluxmeter, was so mounted on a wooden support that it could be set with its axis parallel to that of the compensating coil and its center in the central horizontal line of 148 consecutive turns of the cage which alone were used in this part of the experiment. The test coil was moved along by measured steps from a point near one end of the cage to a point near the other, and in each position the fluxmeter deflections were obtained twice for reversals of the current in the cage; and the procedure was repeated with the coil moving in the other direction. The current remained constant within about one fourth per cent. during the whole process.

The mean fluxmeter deflections were then plotted on cross-section paper as a function of the position of the test coil. In this way it was found that the intensity produced by the cage did not vary by quite as much as 1 per cent. of its mean throughout the region occupied by the main cylindrical part of the rotor, and that it varied only 1.4 per cent. in passing from one end of the rotor to the other end, becoming of course greater as the ends were approached. Over the greater portion of the length of the rotor the intensity did not vary by more than one third or one quarter per cent. The variation would have been slightly less had the 151 turns been used as they were in the rotation experiments.

§27. The compensating cage (with 151 turns) was now mounted over the rotor and its coil, the centers of all three being made nearly coincident. The cage was adjusted with the longer edges parallel to the rotor and its axis parallel to the earth's intensity, and was clamped to the floor in this position. The cage current necessary to compensate the earth's intensity was then determined. With this end in view, a bunched longitudinal coil of thin insulated copper wire had been wound over the central four tenths of the rotor, two sides of the coil being diametrically opposite to one another, and the other two being semicircular and on the same side of the rotor. This coil was connected in circuit with the fluxmeter and set with its axis parallel to the axis of the cage and to the earth's intensity. Turning the rotor through 180° produced a deflection of 17.3 cm. with no current in the cage. With a current of 335 milliamperes in the proper direction in the cage, the deflection on reversal was not 0.1 mm. This current, therefore, compensated the earth's intensity through the central region of the rotor within a minute fraction of 1 per cent., and somewhat less completely throughout the rest of the rotor, as appears from §26.

After the determination of the compensating current the longitudinal test coil was removed from the rotor, and the fluxmeter and rotor and compensator coils connected for the main experiments.

§28. In studying the earth's intensity in the region to be occupied by the rotor it was found that rotation of the fluxmeter through 360° about the vertical in its former position caused the declination to vary through a range of about half a degree. For this reason and because it was desired to have a greater range of scale distances available, the fluxmeter was removed to a very large room adjacent to that in which the rotations occurred, and was again mounted on a slate shelf cemented into the wall. In the later and more precise of the experiments already described the compensation of the fluxmeter drift had been greatly improved by increasing the thermal insulation of many of the junctions of the circuit. For the final work this insulation was still further improved. By taking this precaution, and by working at night, when air currents were reduced, the drift was made so regular (when it did not vanish, as it usually did not) that its compensation was not difficult to make practically perfect. On the other hand the building, though sometimes completely free from vibration, was often disturbed. This however, is by no means so serious a trouble with a compensated fluxmeter as with an instrument whose readings are not permanent; and observations were obtained which were superior to most of those given above.

TABLE II.

Deflections and Speeds. Final Observations and Results.

1915 Date.	Number of Set.	Rotor End *E*.	Compensator End *E*.	Deflection for Negative Rotation (−).	Deflection for Positive Rotation (+).	Differential Deflection (−) − (+).	Zero Correction.	Speed for (−).	Speed for (+).	Mean Speed.	Field Intensity.	Distance from Rotor to Compensator.
				mm.	mm.	mm.	mm.	volts	volts	r.p.s.		m.
March 5	1	2	*B*	−4.7	−3.2	−1.5	−0.6	61	61	34.5	0	1.2
" 5	2	2	*A*	−5.0	−3.3	−1.7	−0.6	65	65	36.8	"	"
" 12	3	2	*A*	−4.9	−3.6	−1.3	−0.6	60	64	35.1	"	"
				(−5.4)[1]		(−1.8)[1]		(64)[1]		36.2		
" 12	4	2	*A*	−5.0	−3.4	−1.6	−0.6	60	60	34.0	"	"
" 13	5	2	*A*	−4.8	−2.7	−2.1	−0.6	64	59	34.8	"	"
				(−4.2)[1]		(−1.5)[1]		(59)[1]		33.4		
" 13	6	2	*A*	−3.2	−1.3	−1.9		63	63	35.7	− *E*	"
" 13	7	2	*A*	−7.2	−5.7	−1.5		66	61	35.9	+ *E*	"
" 16	8	2	*A*	−3.4	−2.1	−1.3	+0.6	61	65	35.7	0	"
				(−4.0)[1]		(−1.8)[1]		(65)[1]		36.8		
" 16	9	2	*A*	−4.3	−2.7	−1.6	+0.6	69	69	39.1	"	"
" 16	10	2	*A*	−1.4	−0.4	−1.0	+0.6	42	41	23.5	"	"
" 16	11	2	*A*	−1.3	−0.5	−0.8	+0.6	40	40	22.6	"	"
" 18	12	3	*A*	+2.5	+4.4	−1.9		70	68	39.1	"	"
				(+2.3)[1]		(−2.1)[1]		(68)[1]		38.5		
" 18	13	3	*A*	+2.4	+4.6	−2.2		70	69	39.3	"	"
				(+2.3)[1]		(−2.3)[1]		(69)[1]		39.1		
" 18	14	3	*A*	+1.9	+4.0	−2.1		70	67	38.8	"	"
				(+1.6)[1]		(−2.4)[1]		(67)[1]		37.9		
" 22	15	2	*A*	−3.9	−1.4	−2.5	+1.2	70	68	39.1	"	1.6
				(−3.6)[1]		(−2.2)[1]		(68)[1]		38.5		

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[1] The quantities in parentheses are the deflections for negative rotations, the differential deflections, and the speeds for negative rotations corrected to the speeds of the positive rotations.

TABLE II.—*Continued.*

1915 Date.	Number of Set.	Rotor End *E.*	Compensator End *E.*	Deflection for Negative Rotation (−).	Deflection for Positive Rotation (+).	Differential Deflection (−) − (+).	Zero Correction	Speed for (−).	Speed for (+).	Mean Speed.	Field Intensity.	Distance from Rotor to Compensator.
				mm.	mm.	mm.	mm.	volts	volts	r.p.s.		m.
March 22	16	2	*A*	−3.9	−1.3	−2.6	+1.2	71	68	39.3	"	"
				(−3.5)[1]		(−2.2)[1]		(68)[1]		38.5		
" 22	17	2	*B*	−3.8	−1.7	−2.1	+1.2	71	71	40.2	"	"
" 22	18	2	*B*	−3.7	−1.5	−2.2	+1.2	72	72	40.8	"	"
" 22	19	2	*A*	−3.7	−1.6	−2.1	+1.2	71	71	40.2	"	"
" 23	20	2	*B*	−0.7	+0.4	−1.1	+1.2	37	35	20.4	"	1.3
				(−0.5)[1]		(−1.0)[1]		(35)[1]		19.8		
" 23	21	2	*B*	−0.8	+0.2	−1.0	+1.2	41	40	22.9	"	"
" 23	22	2	*B*	−0.5	+0.3	−0.8	+1.2	38	38	21.5	"	"
" 23	23	2	*B*	−0.5	+0.4	−0.9	+1.2	37	37	20.9	"	"
" 23	24	2	*B*	−0.6	+0.5	−1.1	+1.2	36	36	20.4	"	"

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[1] The quantities in parentheses are the deflections for negative rotations, the differential deflections, and the speeds for negative rotations corrected to the speeds of the positive rotations.

§29. The results of 24 sets of observations made under the improved conditions are given in Table II. Two sets were rejected because of great difference in the speeds for right handed and left handed rotations; and one set, in the middle of which an accident happened to the turbine, was rejected because of great speed differences and also because it was obtained on an *afternoon*, when the fluxmeter could not be well compensated either for thermal effects in its own circuit or, apparently, for variations of the earth's field (the distance from rotor to compensator on this occasion was about 2.2 meters). The retention of the rejected observations, which were quite consistent with those retained, would not have affected in any way the conclusions to be drawn from the experiments.

For these observations the fluxmeter circuit happened to be connected up in such a way that a negative value of the differential deflection corresponded to an effect in the direction predicted by theory on the assumption that the electrons in revolution are negative. The negative sign here is thus consistent with the positive sign in Table I.

In most of the sets the speeds for the two directions of rotations were nearly the same. When they differed by more than one volt (or about half a revolution per second), except in the case of those observations made in a magnetic field, the deflections for the negative rotation and the corresponding differential deflections, have been reduced to the speed of the positive rotation by the method explained in §32. The reduced values, along with the common reduced speeds are given in parentheses.

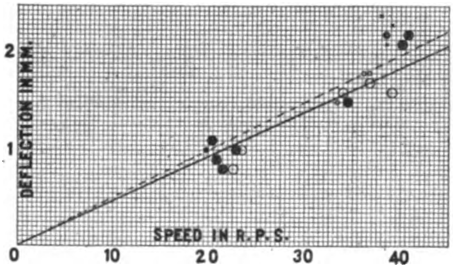

Fig. 6.

Differential Deflection and Speed.

All the deflections were obtained at 8 meters scale distance except those of March 22, which were obtained at 8.7 meters. In the table the deflections for these observations are reduced to 8 meters.

The differential deflection is plotted as a function of the speed in Fig. 6, sets 6 and 7, which were obtained with the rotor in the magnetic field of the earth, or that field reversed, being omitted. The large circles designate the observations which needed no reduction for speed differences; the smaller circles and crosses, those for which reductions were made. The circles designate observations made with end *2* of the rotor east; the white circles corresponding to those made with the compensator end *A* east, the black circles to those made with compensator end *B* east; the crosses designate observations made with the rotor end *3* east and compensator end *A* east.[1]

The continuous straight line in the figure is drawn with a slope obtained by dividing the sum of all the differential deflections for the observations which needed no reductions by the sum of all the corresponding speeds, and thus gives the weighted mean deflection per unit speed, on the assumption of proportionality between them. This quantity is 0.046 mm./r.p.s.

The broken straight line is drawn in the same manner for all the observations made with the earth's intensity compensated, reductions having been made when necessary, as indicated above. From this line, the mean deflection per unit speed is 0.050 mm./r.p.s.

It is clear from the figure that the assumption made above is justified: the deflection is proportional to the speed within the limits of the experimental error. It is also clear that within these limits this deflection is independent of the orientation of the rotor or compensator or the distance between them, this distance being always at least as great as 1.2 meter. The average departure of the differential deflection for a single set from the ordinate of the (broken) straight line corresponding to the speed is 12 per cent.

§30. In the observations just described the readings for zero speed of the rotor throughout each set were, as before, obtained with the rotor set at a definite position angle. The absolute deflection depended upon this setting; but, as has already been said, it was early proved that the differential deflection did not. It was nevertheless considered important to investigate this matter more fully.

For this purpose a permanent bar magnet was mounted so as to be free to rotate in a horizontal plane about a vertical axis passing through its center, and arrangements were made to rotate it at the speed of about 26 revolutions per second by a small alternating current motor at a distance from the magnet and the coils of the fluxmeter circuit. Near the magnet was clamped a small low resistance coil of insulated copper wire connected in the fluxmeter circuit arranged (except for this addition) as in the principal experiments. Another coil, with ten turns of insulated wire, was wound on the compensator close to the coil, and was connected through a key and an adjustable high resistance box with the terminals of a storage battery.

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[1] In the original drawing, in the upper right-hand corner, two small white circles on the same center are shown in place of the smallest of the group of three black circles shown in the reproduction. Also, the second spot in the group appears in the original as a large white circle surrounding a large black circle with the same center.

By means of this coil and battery circuit any desired change of flux could be produced in the fluxmeter circuit; and by means of the rotating magnet and the adjacent coil in the fluxmeter circuit the effect of the iron rotor in sending an alternating current through this circuit, and in producing a motion of the lamp's image up and down on the scale for very slow rotations, could be closely imitated.

The magnet was rotated slowly and the extreme scale readings A and B $(B > A)$ noted. On the magnet's being rapidly rotated the scale reading C always became the mean of the two readings, viz.,

$$\tfrac{1}{2}(A + B).$$

The fluxmeter deflection D produced by closing the battery circuit was determined while the magnet was at rest. Then the circuit was closed, and the magnet driven up to full speed, and the scale reading E determined; then the magnet was brought to rest and set in the position giving one of the extreme scale readings A. It was always found that

$$D = (E - A) + \tfrac{1}{2}(A - B).$$

These observations were made with two quite different values of $A - B$, and two quite different values of D; some of the experiments were made with the battery circuit closed before the rotation of the magnet was started, others with this order reversed. But the result was always the same.

We have thus conclusive proof that, as would be expected, the fluxmeter deflection, when reckoned from the proper zero C, gives correctly the flux changes. If one of the extreme points A or B has been taken as the zero, the true change of flux is given by the above equation.

For most of the observations given above the rotor was set for the zero reading at or close to one of the positions giving the readings A and B, and $A - B$ was determined. The corrections to the true zero C could then be readily made. These corrections are given, for the sets for which they are available, in Table II. This correction is of course of no consequence for the differential deflection, but it affects the absolute deflection greatly.

§31. When the means of the absolute deflections for positive and negative rotations are corrected to the true zero in accordance with the last article and compared with the speeds, a very simple relation is found to exist between them. In Table III. the observations are divided

Table III.

Mean Deflections and Squares of Speeds.

Numbers of Sets.	Sum of Deflections (Observed).	Sum of Deflections (Reduced).	Mean Deflection (Observed).	Mean Deflection (Reduced).	Sum of Speeds Squared (Observed).	Sum of Speeds Squared (Reduced).	Mean Square of Speed (Observed).	Mean Square of Speed (Reduced).	Mean Deflection per Unit Speed Squared (Observed).	Mean Deflection per Unit Speed Squared (Reduced).
1–5, 8–9, 15–19	43.8 mm.	43.7 mm.	3.65 mm.	3.64 mm.	16,920 $(\text{r.p.s.})^2$	16,870 $(\text{r.p.s.})^2$	1,410 $(\text{r.p.s.})^2$	1,406 $(\text{r.p.s.})^2$		
10–11, 20–24	9.4	9.3	1.34	1.33	3,320	3,290	474	471		
1–5, 8–9, 10–11, 15–19, 20–24	53.2	53.0			20,240	20,160			$\frac{\text{mm.}}{(\text{r.p.s.})^2}$ 0.00263	$\frac{\text{mm.}}{(\text{r.p.s.})^2}$ 0.00263

into two groups, those at lower speeds and those at higher speeds, and for each group are given the sum of the observed deflections and the mean deflections (both corrected to the true zero), the sum of the squared speeds, and the mean of the squared speeds; while for both groups together there is given the quotient of the sum of the deflections by the sum of the squared speeds, or the mean deflection per unit speed squared, all quantities being given both as observed and also as reduced to the same speed for both directions of rotation.

In Fig. 7 the mean squared deflections for the two groups are plotted as a function of the mean squared speed. The straight line is drawn

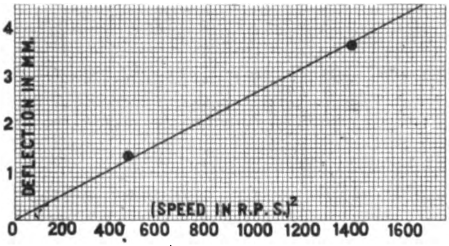

Fig. 7.

with the slope given by the last two columns in the table, which is identical for both observed and reduced quantities, as are the mean deflections within the experimental error. The figure shows that within the limits of the experimental error the absolute deflection is proportional to the square of the speed.

§32. The method of reducing a deflection observed at one speed to the deflection which would have been produced at another, and thereby correcting the differential deflections obtained when the speed for left hand rotations did not equal that for right hand rotations can now be readily explained. If we denote by D the deflection (from the true zero) obtained for a speed S, and by D' the deflection which would have been obtained for a speed S' near S, we have

$$D = aS + bS^2$$

and

$$D' = aS' + bS'^2,$$

where a and b are constants known very approximately from the observations which needed no correction. The correction, or small quantity which must be added to D, is

$$D' - D = a(S' - S) + b(S'^2 - S^2).$$

From Fig. 6 we get

$$a = \pm \tfrac{1}{2} \times 0.046 \frac{\text{mm.}}{\text{r.p.s.}} \quad \text{or} \quad \pm 0.013 \frac{\text{mm.}}{\text{volt}},$$

and from Fig. 7 we get

$$b = \pm\, 0.00263 \frac{\text{mm.}}{(\text{r.p.s.})^2} \quad \text{or} \quad \pm\, 0.00084 \frac{\text{mm.}}{(\text{volt})^2}.$$

As an example, what precedes may be applied to set 5, Table II., to reduce the deflection for left handed or negative rotations at speed 64 volts to the speed of 59 volts. In this case we have

$$D' - D = \{ -0.013(59-64) - 0.00084(59^2-64^2)\}\ \text{mm.} = +\, 0.6\ \text{mm.}$$

By adding this quantity to the observed deflection − 4.8 mm., and subtracting − 2.7 mm., we obtain the differential deflection − 1.5 mm. for the speed 59 volts.

In this way all the differential deflections given in parentheses in Table II. were obtained. The total correction being always small, it is not important that the values of a and b should be accurately known. By using *all* the differential deflections for zero intensity of field, reduced in this manner when necessary, we obtain a more nearly correct value of a, viz.: $a = \pm\, 0.025$ mm./r.p.s., corresponding to the slope of the broken line in Fig. 6.

§33. The intensity of the magnetic field in which the rotor moved having been reduced in the final experiments to a minute portion of the earth's intensity, it is clear that that part of the deflection which is proportional to the square of the speed, or the mean deflection, is not produced by induced currents in the rotor.

The proportionality of the deflection to the square of the speed, and the reversal of the deflection with the reversal of the rotor, strongly suggest that the effect is due to the radial expansion (and accompanying longitudinal contraction) of the rotor produced by its rotation.

It has long been known that the longitudinal magnetic flux through an iron rod in or out of a longitudinal field is altered by the application or removal of longitudinal tension;[1] and that the longitudinal flux through the walls of an iron tube in a longitudinal field is altered by radial expansion or contraction produced by the application of hydraulic pressure from within or its removal.[2] The application and removal of longitudinal tension produce opposite effects; likewise radial expansion and contraction produce opposite effects. But longitudinal contraction and radial expansion produce effects of the same sign.[2]

Most of the experiments on this subject have been made on iron wires or cylinders in longitudinal fields, only a few having been made on iron rods with residual (or permanent) magnetization. For permanently magnetized iron rods Matteucci[1] and Villari[1] found that elongation produced an increase of flux in the case of soft iron, but a decrease in the case of hard iron or steel. All gradations were found to exist between the two extremes.

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[1] Ch. Matteucci, Ann. de chim. et de phys. (3), 153, 1858, p. 416; E. Villari, Pogg. Ann., 126, 1865, p. 87.

[2] W. Thomson, Roy. Soc. Phil. Trans., 170, 1880, p. 64.

In all of the very numerous experiments made with the two different rotors A and B used in this work, with the exception of one set mentioned below (§34), the mean deflection produced by rotation was in the direction indicating that the longitudinal flux through the rotor was *increased.* To test the above explanation of the effect it was necessary, on account of the dependence of the known mechanical effect upon the nature of the rod and perhaps upon the intensity of magnetization, to make direct experiments on the effect of *longitudinal compression* (and its removal) on the magnetization of the two rotors. The residual flux density in the central section of rotor A was about 7 maxwells per cm.^{2}; that in rotor B about 4 maxwells per cm.^{2}

Each rotor in turn was therefore placed in a strong wooden frame constructed for the purpose, and longitudinal compression was applied by means of a brass screw working in a brass nut and operated with a brass wrench. With the fluxmeter and coils arranged as in the principal experiments and the axes of the rods in the magnetic equator, it was repeatedly verified that *compression increased* the magnetic flux through the rod, and that removal of the compression brought the flux back to its initial value. In the case of rod A, 4 or 5 cm. deflection was produced by a half-turn of the screw; in the case of rod B the deflection produced by a half-turn was 3 or 4 cm. These experiments thus confirm the explanation given above of the mean deflection produced by rotation.

A part of the effect may be due to possible unsymmetrical distribution of the rotor's mass about its axis and consequent centrifugal distortion. This also would give an effect proportional to the square of the speed. Experiments in which rotor B, with ends fixed, was subjected to a lateral force of about 150 lbs. near one end of its coil gave a deflection of a few mm. in the direction indicating increase of magnetic flux when the force was applied and decrease when it was removed.

§34. The apparently exceptional set of observations referred to above, in which the mean deflection appeared to indicate a diminution of magnetization, was made over a year ago with rotor A. When the magnetization of this rotor was reversed, as it was thought, the deflection remained exactly the same. The reversing magnetic intensity applied, however, was small; and in view of the well-known van Waltenhofen phenomenon it is quite possible that true reversal did not occur. The direction of the magnetization was tested, but only by noting the direction of the deflection when the rod was smartly tapped, a test which has not always been found conclusive. A conclusive test is always to determine the direction of the fluxmeter deflection on the removal of the rod from its coil. This same result was obtained in the preliminary observations made in Louisiana, with a rod about half as long. To this, however, but little weight can be attached.

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[1] Ch. Matteucci, Ann. de chim. et de phys. (3), 153, 1858, p. 416; E. Villari, Pogg. Ann., 126, 1865, p. 87.

Anomalous effects of perhaps the same kind were noted by Villari (l. c.) in the case of longitudinal tension. He found that it was possible by magnetizing a steel rod with a current in one direction, and then with a weaker current in the opposite direction, to make it behave like iron—so that elongation increased its magnetization instead of decreasing it.

The exceptional cases mentioned therefore do not invalidate in any way the explanation of the mean deflection presented in the last article. It is of course not credible that reversal of the magnetization throughout a rod should have a different effect on the deflection produced by rotation from that of simply reversing the rod, an extraneous field being excluded as in the final experiments described here.

§35. In connection with the Louisiana experiments one of my friends suggested that the effects might be due to torsion, but was inclined to withdraw his suggestion when he found that the rotating rod was about 7 cm. in diameter.

In the case of a permanently magnetized rod of soft iron, according to the experiments of G. Wiedemann,[1] opposite small twists produce equal and opposite reversible effects on the magnetization.[2] It follows from this that the differential deflection would be increased by torsion for one orientation of the rotor, and decreased by the same amount for the opposite orientation. The experiments show, as would be expected, no difference produced by such a reversal.

Some direct experiments on rotor *B* confirmed Wiedemann's statements. For a torque of about 20 lb.-ft. applied to one end of the rotor while the other end was clamped, a mean deflection of about 2 mm. was produced. Experiments were made with both orientations of the rotor and for both directions of twist.[3] When the rotor was running at a speed of 38 r.p.s. in the principal experiments, the torque applied to one end of the rotor by the driving rod was only 1.1 lb.-ft., and the other end of the rod was of course free, except for the frictional torque. The effect of torsion on any of the deflections observed in the experiments on rotation must thus have been far less than the smallest readable quantity.

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[1] G. Wiedemann, Elektricitaet, III., p. 676.

[2] The effects are similar in the case of steel except that hysteresis also occurs.

[3] Wiedemann does not give the direction of the effect. My experiments gave a diminution of flux when the positive end of the rod was twisted clockwise relative to the negative end to one looking along the rod from the negative to the positive end.

§36. As a result of all that precedes we are forced to the conclusion that the rotation of a rod of steel[1] produces therein an intrinsic magnetic intensity proportional to the angular velocity and acting in a direction opposite to the intensity which would be produced by an electric current flowing around the rod in the direction of rotation, as required by the theory proposed in §§1 and 5.

To obtain the intrinsic magnetic intensity per unit speed it is now necessary only to multiply half the mean differential deflection per unit speed, given in §29, by the intrinsic intensity per unit deflection, H_0, given in §12. In this way we obtain

$$\frac{H}{n} = -\tfrac{1}{2} \times 0.050 \frac{\text{mm.}}{\text{r.p.s.}} \times 1.26 \times 10^{-5} \frac{\text{gauss}}{\text{mm.}} = -3.1_5 \times 10^{-7} \frac{\text{gauss}}{\text{r.p.s.}}. \quad (13)$$

Similarly, from §§29 and 13, we obtain for the magnetic flux-density per unit speed produced by the intrinsic intensity of rotation in the central part of the rotor, the quantity

$$-\tfrac{1}{2} \times 0.050 \frac{\text{mm.}}{\text{r.p.s.}} \times 7.7 \times 10^{-4} \left(\frac{\text{maxwells}}{\text{cm.}^2}\right) \text{per mm.}$$

$$= -1.9 \times 10^{-5} \left(\frac{\text{maxwells}}{\text{cm.}^2}\right) \text{per r.p.s.}$$

This quantity divided by 4π gives an approximate value of the intensity of magnetization at the center of the rotor per unit speed, viz.,

$$-1.5 \times 10^{-6} \text{ c.g.s. unit per r.p.s.}$$

The magnitude of H/n given in equation (13) as a result of the last series of experiments is, within the experimental error, equal to one half the maximum value computed in equation (9) on the assumption that negative electrons alone are effective. The same is true of the result of the earlier observations given in §24.

§37. For the same intrinsic magnetic intensity of rotation and the same material, the intensity of magnetization depends upon the shape of the rotating body and is less for a sphere than for a long cylinder.

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[1] In the experiments of Lebedew (Ann. der Phys., 39, 1912, p. 840) the magnetic effect of rotating at high speed anyone of the several *non-magnetic* substances tried was nil, in conformity with the theory set forth in this paper. Lebedew's experiments were performed for a different purpose from that of this investigation, their object being to study the effect of centrifugal electron displacement, and the data he gives are insufficient for an exact calculation of the superior limit they give for the effect considered here. An approximate calculation, however, can be made and shows that the intensity of magnetization produced in Lebedew's non-magnetic bodies was not greater than about one hundredth of the value here obtained for steel, reduction being made to the same speed.

The earth's intensity of magnetization is about 0.08 c.g.s. unit, and its angular velocity is 1/86,400 r.p.s. If therefore our iron were spherical in shape and rotating at the speed of the earth, its intensity of magnetization would be less than the fraction $\frac{1.5 \times 10^{-6}}{86,400 \times 0.08}$, or 2×10^{-10}, the earth's intensity of magnetization.

Inasmuch, however, as we have no knowledge of the magnetic behavior of any substance under the conditions prevailing at more than a very small distance within the surface of the earth, it is still possible that this effect, which has the same sign as the earth's magnetization, may also account for its magnitude. It seems probable, however, that at least two other effects are prominently involved, viz., the centrifugal displacement and the thermionic displacement of electrons, which give, when rotation occurs, magnetic intensities in the direction required.

§38. SUMMARY.

1. On the electron theory it is shown that by a sort of molecular gyroscopic process a body of any substance set into rotation becomes the seat of a uniform intrinsic magnetic intensity parallel to the axis of rotation, proportional to the angular velocity, and (like the magnetization of the earth and the sun) directed, provided the effect of the negative electrons is preponderant, oppositely to the intensity which would be produced by an electric current flowing around the body in the direction of rotation. If the substance is magnetic, magnetization results; otherwise not. If only the negative electrons are involved, the intensity per unit speed has its maximum numerical value and is calculated to be

$$\frac{H}{n} = -7.1 \times 10^{-7} \frac{\text{gauss}}{\text{r.p.s.}}.$$

2. The theory of the converse effect (rotation by magnetization) is developed in a very simple manner.

3. An extended series of experiments on the magnetization of steel rods by rotation is described. All suspected sources of systematic error have been eliminated by the elaborate precautions taken, and it is believed that the effect predicted by theory has been discovered. The method of electromagnetic induction was used, a fluxmeter, whose deflections were read to tenths of mm. at the scale distance 8 m. (usually), being the chief measuring instrument. The intrinsic magnetic intensity of rotation, and the change of magnetic flux density, per unit speed were found to be about

$$-\ 3.1 \times 10^{-7}\,\frac{\text{gauss}}{\text{r.p.s.}}$$

and

$$-\ 1.9 \times 10^{-6}\left(\frac{\text{maxwells}}{\text{cm.}^2}\right)\text{ per r.p.s.,}$$

respectively. Experiments made by Lebedew for a different purpose are quoted as showing that non-magnetic substances are not magnetized by the process by which iron is here shown to be magnetized.

4. Experiments, incidental to the work, on the use of a fluxmeter when unidirectional and alternating flux changes occur either alone or superposed, and in the change of residual magnetization by torsion, are described.

5. Together with the change of flux proportional to the speed, another change proportional to the square of the speed has been found and accounted for by the radial expansion of the rod produced by rotation. In support of this view experiments are described in which the change of (residual) longitudinal flux through the rods was determined when the rods were longitudinally compressed and when the stress was removed.

6. The intensity of magnetization produced in the rotating iron per unit speed was about 1.5×10^{-6} c.g.s. unit per r.p.s. If the rod had been rotated at the speed of the earth, viz., 1/86,400 r.p.s., its intensity of magnetization would have been about 2×10^{-10} that of the earth. This, however, does not prove that the earth's magnetization may not be due largely to the effect in question, as we are entirely ignorant of the magnetic properties of all substances under the conditions prevailing within almost the whole of the earth. Other causes are mentioned as probably accounting for at least a part of the earth's magnetism. Schuster has suggested that an effect of the sort chiefly investigated in this paper may explain the secular variation as well as the mean magnetization of the earth.

I am indebted to Mrs. Barnett for a great deal of help throughout the experimental part of this work, and to Mr. Arthur Freund, mechanician in this laboratory, for constructing most of the special apparatus and for other mechanical assistance.

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ELECTROSTATIC MEASUREMENT OF ELECTRODE POTENTIALS.

By Arthur W. Ewell.

THE determination of the difference of electrical potential of two electrodes dipping in a common electrolyte is simple and can be accomplished with a high degree of accuracy by several well-known methods. Measurement of the absolute potential difference between a single electrode and the electrolyte is difficult and the various methods which have been employed have yielded widely differing results.[1] Excellent bibliographies of this entire subject are accessible[2] and will not be repeated here. The papers of Borelius and Guyot referred to later are the only important memoirs which have appeared since these compilations.

Historical.

The different experimental methods for determining electrode potentials may be classified respectively as electro-capillary, endosmotic, capacity and electrostatic.

Mercury is naturally the electrode which has been employed for electrocapillary methods. Assuming that the absolute potential difference between mercury and an electrolyte results in the formation of a Helmholtz "double layer" which reduces the surface tension, Ostwald and others have concluded that when mercury in a capillary tube shows maximum surface tension the double layer is absent and that therefore the applied potential required to give the maximum surface tension is equal and opposite to the natural potential difference between mercury and the electrolyte. By somewhat similar reasoning mercury breaking into fine drops at the surface of the electrolyte was assumed to come to the same potential as the electrolyte and therefore the difference of potential between the reservoir supplying the drops and the mercury collecting at the bottom of the electrolyte was the absolute potential sought. The results by the two methods agree closely and give for the absolute potential, if the solution contains normal concentration of mercury ions, about 1.05 volts, or when combined[1] with a "normal calomel electrode" give for the absolute potential of the latter 0.593 volts, the mercury of the electrode being positive with reference to the solution.[2]

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[1] "Wir gegenwartig über die Komponenten der electromotorischen Kraft eines Elementes einfach gar Nichts wissen" (Chwolson).

[2] Palmaer, Zeit. f. phys. Chem., 59, 129, 1907. Potentialkommission d. deutsch. Bunsen Gess., Zeit. f. Electrochemie, 50, 818, 1908. Chwolson, Lehrbuch d. Physik, IV., I., 228, 1908.

Endosmotic methods have been chiefly developed by Billitzer.[3] He observed the motion of fine wires suspended in an electrolyte between parallel plate electrodes and also the motion of colloidal particles which dropped between the plates. The concentration of the electrolyte was varied until a difference of potential applied to the plates produced no motion of the wires or the particles and he concluded that they were then at the same potential as the solution. These experiments, with others of a similar nature, gave for the absolute potential of the tenth normal calomel electrode −.125 volt, the negative sign signifying that the mercury was at a lower potential than the calomel solution. Billitzer also obtained approximately the same results by methods depending upon the change of concentration in the vicinity of a dropping electrode, motion of a mercury meniscus, and motion of the electrolyte.

The results of Billitzer differed so greatly from the values given by capillary and dropping electrodes that portions of his work were repeated by Whitney and Blake,[4] and Goodwin and Sosman.[5]

These investigators either failed to obtain his results or interpreted them differently. Later Freundlich and Mäkelt[6] succeeded in duplicating certain of Billitzer's determinations, but failed to obtain his values when the conditions were somewhat varied. Billitzer answered these criticisms with explanations of their failures and arguments for the validity of his original results. He ascribed the difference between his values and those obtained by capillary electrodes to direct or indirect dependence of the surface tension upon the applied potential resulting in the maximum surface tension appearing not when electrode and electrolyte are at the same potential but when the electrode is at about 0.7 lower potential.[7]

The third method for evaluating absolute electrode potentials is also due to Billitzer,[8] and is based upon the assumption that changes in the potential difference between the two elements of the electrode-electrolyte interface will produce changes in the distance between the two oppositely charged layers and consequently changes in the capacity. Billitzer found evidence in the works of Scott[1] and Kruger[2] of marked abnormality in the capacity at the potential which he had determined as the absolute potential by endosmotic methods. The writer, however, after careful study of the original observations is not convinced that these abnormalities are demonstrated beyond the limits of experimental errors.

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[1] If one single electrode potential is determined absolutely with reference to a particular electrolyte any other electrode may also be inserted in the electrolyte and its potential determined from the absolute potential of the first and the difference of potential of the two.

[2] Palmaer, Zeit. f. phys. Chem., 59, 129, 1907.

[3] Drude's Ann., II., 902, 1903. Zeit. f. phys. Chemie, 48, 513, 542, 1904; 48, 624, 1903.

[4] Jour. Am. Chem. Soc., 26, 1339, 1904.

[5] PHYS. REV., 21, 129, 1905.

[6] Zeit. f. Electrochemie, 15, 161, 1909.

[7] Zeit. f. phys. Chemie, 51, 167, 1905. Zeit. f. Electrochemie, 12, 281, 1906; 14, 624, 1908; 15, 439, 1909.

[8] Zeit. f. phys. Chemie, 51, 167, 1905.

The fourth method of determining absolute electrode potentials consists in direct electrostatic measurement. A large amount of work was done by this method previous to 1890, references to which may be found in the bibliography in Chwolson.

The observations of Exner and Tuma[3] were the only ones which were reproduceable and fairly consistent, *i. e.*, which gave for two different electrodes values of the absolute potentials whose algebraic difference was their known potential difference. Their method was similar to Kelvin's water dropper with the water replaced by mercury and the cylinder lined inside by filter paper saturated with the electrolyte which was connected by a wick with the electrolyte in which the electrode dipped. Their results were in rough agreement with those of Billitzer. Certain assumptions in their method may however involve serious systematic errors, which are about to be investigated in this laboratory. The only recent electrostatic work known to the writer is a paper by Borelius describing measurements of the relative, not absolute, potentials in the vicinity of an electrode and its electrolyte.[4]

This uncertainty in the absolute values of electrode potentials led the writer to begin several years ago an attempt to obtain accurate and reliable measurements by electrostatic methods. The final apparatus alone will be described and only the observations made during the past eight months will be presented.

APPARATUS.

Fig. 1 is a schematic sketch of the final apparatus. The electrolyte was usually contained in a flask *A*, 50 to 150 cm.^{3} capacity mounted on a platform supported by legs *a* of fused quartz. The outside of the flask except the neck was coated with a thin metallic film to which connection was made by the wire *b*. The latter could either be connected by the movable wire *c* to the Dolezalek electrometer *C* or, by the movable wire *d* with the wire *e* which could be connected to the earth or to a source of known potential. The portions *f* of the threads by which *c* and *d* were raised and lowered were of fused quartz. The entire apparatus including the water battery *g* for charging the electrometer needle was surrounded by grounded wire netting. The electrode *B* (about 1 mm. in diameter) could be moved up and down and was usually grounded.

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[1] Wied. Ann., 67, 388, 1899.

[2] Zeit. f. phys. Chemie, 45, I., 1903.

[3] Wien. Akad. Sitz. Berich., 97, 917, 1889.

[4] Ann. d. Physik, 42, 1129, 1913.

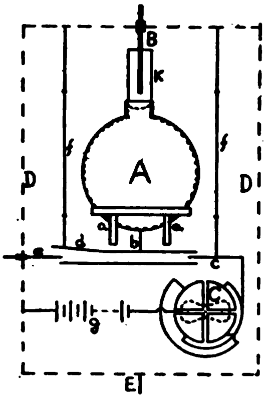

Fig. 1.

The theory of the method was as follows: If the electrolyte was initially at zero potential, upon introduction of the earthed electrode *B* it would acquire a potential equal to its natural absolute potential with reference to the particular electrode. A charge at somewhat different potential would be induced upon the metal film upon the outside of *A*, the deflection of the electrometer would be proportional to this potential, and, by a calibration described later, the potential of the electrolyte could be ascertained.

The procedure of an observation was as follows: The electrometer and the outside of the flask were earthed by the wires *b*, *c*, *d* and *e*, the latter being connected to earth. The electrolyte was poured into *A*. The neck *k* and the legs *a* were then cleansed with dilute alcohol and heated with a Bunsen burner to remove any moisture. The earthed electrode *B* was then lowered until it dipped in the electrolyte and immediately withdrawn. No readings were taken because the introduction of the electrolyte and the heating of the neck often produced static charges of many volts potential. After standing undisturbed several hours *d* was disconnected from *e*, and the electrometer reading was observed on a scale 160 cm. from the mirror. The earthed electrode *B* was then lowered until it dipped in the electrolyte and the accompanying deflection of the electrometer was observed from which, as explained later, the absolute potential of the electrolyte was calculated.

The following readings are those of a typical experiment.

Oct. 5, 1914. Flask *e*[1]. Normal $ZnSO_4$ solution.

Electrometer Readings.

After heating neck and legs	49.5
Outside film and needle earthed	48.1
Outside film and needle insulated.	
Earthed zinc electrode dipped in electrolyte	39.9
One minute later	40.0
Fourteen minutes later	40.2
Thirty-two minutes later	41.0

---

[1] See below.

Sources of Error.

1. *Poor Insulation.*—The loss of charge rarely exceeded 2 per cent. per minute. Since the complete period of the electrometer needle was about four seconds and its motion was considerably damped, a reading required only a small fraction of a minute. Occasionally the leakage was excessive and the observation was rejected. If the metal film on the outside was different from the electrode and the electrolyte had stood for some days in a glass flask there was occasionally evidence of conduction through the glass. When such conductivity was present the electrometer would not at once come to a definite reading when the earthed electrode was introduced but slowly drifted, and the final resting point of the needle when the electrode was left in the electrolyte differed from the zero position. Also there was a slow drift to this latter position if the needle was momentarily earthed and then insulated, the electrode remaining in the electrolyte. Quartz flasks never showed such conductivity. In particularly cold, dry weather surface leakage was inappreciable, but such static charges appeared when any part of the apparatus was disturbed that observations were impossible.

2. *Volta Effects.*—We are seeking the absolute difference of potential between an electrode and the surrounding electrolyte. The writer believes that the apparatus and procedure outlined above eliminates so-called Volta potentials or effects due to possible differences in potential in the air immediately surrounding electrode and electrolyte. As proof of the correctness of his belief, the electrolyte was successively replaced by mercury in each of the flasks employed and the deflections of the electrometer were observed when earthed wires of different metals (Cu, Ag, Zn, Ni, Fe) were dipped into the mercury. In every case the potential observed was less than 0.1 volt and usually it was inappreciable.

3. *Initial Static Charges on Electrolyte.*—As mentioned above, such charges were usually observed when the flask was first filled and the neck of the flask was heated. It was assumed that after several hours these static charges largely disappeared and that the potential of the electrolyte differed little from zero (the potential of the cage). The deviations in the observations are probably largely attributable to this cause. It was not possible to further reduce errors from this source by delaying observations because errors of the first type usually began to appear. The fact that mercury in the different flasks and with different electrodes showed practically no potential is further evidence against this source of error being serious. ?

4. *Influence of Material of Flask and Metal Film.*—To eliminate any such specific influence different materials were used which are designated as follows in subsequent tables.

a = quartz flask No. 1 with outside film of silver.[1]
b = quartz flask No. 1 with outside film of aluminum.[2]
c = quartz flask No. 2 with outside film of silver.
d = quartz flask No. 2 with outside film of aluminum.
e = glass flask No. 1 with outside film of silver.
f = glass flask No. 1 with outside film of aluminum.
g = glass flask No. 2 with outside film of silver.
h = glass flask No. 2 with outside film of aluminum.

Observations with paraffin coated vessels and vessels of other shapes are described later.

EXPERIMENTAL RESULTS.

The following table gives all the observations made during the past months with narrow neck flasks with the final form of apparatus except a few observations which were discarded because of evidence of errors of the first type mentioned above. At the foot of each column is stated the mean with its probable error, except for Cu – $CuSO_4$ where the variation in the readings is so great that little quantitative importance can be given the results.

CALIBRATION.

The algebraic difference in the mean deflections for zinc and silver is 11.67. The difference of potential of zinc and silver electrodes, each in a normal solution is 1.541 volts.[3] Dividing one by the other gives 7.50 divisions per volt as the calibration constant of the system. This constant was checked by substituting mercury for the electrolyte and observing the electrometer deflection due to the charge induced on the outside of the flask when the potential of the mercury was changed by known steps by means of the electrode *B*.

This method of calibration gave values for this constant, which for narrow neck vessels were often as much as 15 per cent. greater than the values calculated as just described while for wide necked vessels (see below) both methods of calibration gave almost identical results. This difference was to be expected since the outside metallic coating was nearer the wire when the neck was narrow and this wire had a like charge in the direct calibration with mercury and a charge of opposite sign in the method of calibration by known differences of potential, and in all the actual experiments. The mercury calibration proved that the deflection of the electrometer was proportional to the potential within 0.2 per cent. up to 1.43 volts and that there was no appreciable asymmetry in the deflections on the two sides.

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[1] Chemically deposited upon flask.

[2] Aluminum foil attached by a very thin film of shellac.

[3] Wilsmore's Tables, Winkelmann's Handbuch, IV., I., p. 856.

Table I.

Zn $n\,ZnSO_4$	Ag $n\,AgNO_3$	Cu $n\,CuSO_4$	Zn $n/2\,H_2SO_4$	Cu $n/2\,H_2SO_4$
a +7.8	*a* −2.0	*a* 0.0	*a* +9.2	
" 6.3	" .5	" +2.3	" 7.0	*a* +2.2
" 6.0	" 3.5	" + .8	" 8.7	" 0.0
" 8.8	" 3.5	*e* +3.0	" 8.3	" +3.5
" 9.1	" 4.3	*g* + .3	*e* 9.7	" +2.1
" 7.3	" 3.6	" +1.1	" 9.3	" +1.1
b 8.0	" 3.0	*f* −2.9	" 9.2	" − .8
" 7.9	" 2.8	" −2.3	" 8.8	" − .3
" 8.4	" 2.8	" − .5	" 7.9	" + .2
c 7.0	" 2.4	*c* − .3	*f* 7.6	*e* +1.0
" 7.4	*b* 2.0		" 7.7	" +1.1
" 6.5	" .7		" 7.6	" +1.2
g 8.2	" 3.2		*g* 8.8	" + .6
f 10.6	" 3.5		" 8.7	" + .7
" 6.9	" 3.0		" 8.7	*f* − .8
g 8.5	" 4.7		" 11.6	" − .8
" 9.6	" 4.4		" 10.9	" − .7
" 9.0	" 3.3		" 8.1	*g* + .5
" 8.0	*e* 5.4		" 7.1	" + .4
" 9.2	" 4.9		" 10.2	" + .4
f 7.7	" 4.8		" 9.2	" +3.1
" 6.3	*f* 3.1		" 9.3	" +2.9
c 7.2	" 8.3		" 9.6	" +1.3
	h 2.4		*f* 6.5	" +1.0
	g 1.8		" 7.3	" +1.4
	f 6.8		" 8.7	" +2.5
	" 7.3		" 5.5	" +1.8
	" 4.6		" 5.4	" +2.3
	c 4.1		" 5.7	*f* −1.5
			" 5.7	" − .7
			" 7.3	" −2.1
			" 7.2	" −2.5
				" −2.3
				" −1.9
				" −2.0
				" − .3
				" − .2
+7.90±.16	−3.67±.19	+0.18	+7.84±.20	+0.37±.19

Final Results.

Dividing the mean deflection by this constant 7.50 we find for the potential of zinc in normal zinc sulphate solution − 1.05 ± .02 volts, and for zinc in half normal sulphuric acid solution − 1.04 volts. For silver in normal silver nitrate solution we find + .49 ± .03 volt and for copper in normal copper sulphate solution — .02 volt and in half normal sulphuric acid solution — .05 volt.[1]

Observe that these results are mutually consistent. The respective potentials of zinc and copper are very nearly the same in both electrolytes, as would be expected. The differences of potential of copper and zinc are 1.07 and 1.09 volts respectively which compare well with the difference of 1.099 in Wilsmore's table.

WIDE NECK VESSELS.

To make certain that the results were not influenced by the degree to which the outside metal film approached a "closed" conductor, observations were made both with test-tubes 2.5 cm. in diameter 20.5 cm.

TABLE II.

Test-tube.	Beaker.	Test-tube Covered Inside with Paraffin.
Ag. — 4n $AgNO_3$		Ag — n $AgNO_3$
3.1	3.8	4.0
3.6	3.6	5.0
3.2	4.0	4.3
3.6	3.2	3.4
3.4	3.3	3.9
3.3	3.0	4.1
3.3	——	3.4
3.6	Mean, 3.48	2.7
4.2	(0.40 volts)	——
3.2		3.85
——		(0.50 volts)
Mean, 3.47		
(.38 volts)		
Zn — 2.5n $ZnSO_4$		Zn — n $ZnSO_4$
9.9	11.6	8.1
10.8	9.9	7.9
11.1	8.8	8.2
11.1	——	——
10.6	Mean, 10.1	Mean, 8.1
10.1	(1.15 volts)	(1.05 volts)
10.1		
10.4		
11.0		
——		
Mean, 10.5		
(1.16 volts)		

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[1] The signs in Table I. apply to the electrolyte since its potential rather than that of the electrode was under observation. The electrode potential will obviously have the opposite sign.

long, covered with an outside silver film for 7.5 cm. from the closed end, and with a beaker about 7 cm. high, 4 cm. in diameter at the top and 3 cm. in diameter at the bottom with an outside silver coating extending to within about 3.5 cm. of the top. One test-tube was covered upon the inside with paraffin to secure further evidence that the results were independent of the insulating medium. The electrometer readings are given in Table II.

The potentials stated in parentheses were calculated as explained above. Allowing for the difference in concentration, they agree closely with the previous results and show that the values obtained are independent of the shape of the vessel. The results in the last column show that a coating of paraffin inside the vessel does not affect the potential. Similar observations were made with a number of other test-tubes with like results. Further experimental confirmation of certain of the above figures will be found when considering the effect of concentration. Table III. gives a comparison of the writer's results with the values commonly found in tables (Wilsmore's) except that the latter are decreased by .04 volt to correspond to Palmaer's more recent value of the potential of the tenth normal calomel electrode (.573 volt in place of Wilsmore's value of .613).

TABLE III.

	n/10 Calomel Electrode.	Silver.	Zinc.
Wilsmore and Palmaer	+.573	+1.008	− .533
Ewell	(+.06)	+ .49	−1.05

INFLUENCE OF CONCENTRATION OF ELECTROLYTE.

The final form of apparatus is illustrated in Fig. 2. The glass flasks *A* and *A′* contained two concentrations of the same electrolyte. The silver film on the outside of one flask was connected to one pair of quadrants of the electrometer and the other film to the other pair of quadrants. The wires *b*, *b′* permitted grounding of the films and quadrants. An observation was preceded by preliminary steps similar to those previously described. The deflection of the electrometer was observed when one earthed electrode *B* was dipped into the electrolyte and

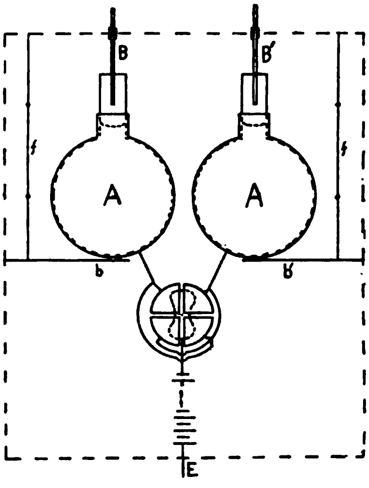

Fig. 2.

then when the other electrode *B′* was also dipped into the other electrolyte. From the deflection with both earthed electrodes in their respective solutions the difference of potential of the two electrolytes was determined. Lack of symmetry was eliminated by changing the order of introduction of the electrodes and by exchanging the two concentrations of the solution between the two flasks. Table IV. gives the final readings with silver nitrate and zinc sulphate.

TABLE IV.

Electrode.	Electrolyte.	Deflection of Electrometer upon Dipping Earthed Electrode into Flask Connected with		Both Electrodes in their Respective Solutions.
		First Pair of Quadrants.[1]	Second Pair of Quadrants.	
Ag.	4*n* $AgNO_3$ in first flask	−3.1	+4.4	+1.3
		−2.2	+2.7	+ .5
	n/250 $AgNO_3$ in second flask	−2.5	+4.3	+1.8
		−3.2	+3.6	+ .4
		−2.6	+3.2	+ .6
		−2.6	+2.8	+ .2
		−1.8	+2.9	+1.1
	n/250 $AgNO_3$ in first flask	−2.9	+ .8	−2.1
		−2.7	+1.7	−1.0
	4*n* $AgNO_3$ in second flask	−2.1	+1.4	− .7
		−3.0	+2.5	− .5
		−1.7	+ .9	− .8
		−3.6	+2.9	− .7
Zn.	2*n* $ZnSO_4$ in first flask	+4.7	−3.4	+1.3
		+5.2	−4.0	+1.2
	n/500 $ZnSO_4$ in second flask	+5.1	−4.0	+ .9
		+5.7	−4.5	+1.2
		+5.0	−3.9	+1.1
		+5.4	−4.6	+ .8
	n/500 $ZnSO_4$ in first flask	+3.7	−5.0	−1.3
		+4.4	−5.0	− .6
	2*n* $ZnSO_4$ in second flask	+4.0	−4.8	− .8
		+3.8	−4.9	−1.1
		+2.9	−4.4	−1.5

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[1] The first pair of quadrants is the pair to which the flask was connected in the work described earlier, and the first flask is the flask connected to these quadrants.

The lower concentration of silver nitrate gives the greater deflection the mean excess being 0.90 which divided by 7.50 gives 0.12 volt. The sign of the deflection shows that the weaker solution is at a lower potential, and therefore a silver electrode in 4*n* $AgNO_3$ solution in a glass vessel is about 0.1 volt lower potential than a silver electrode in *n*/250 $AgNO_3$ solution.

A concentration cell

$$Ag - 4n\ AgNO_3 - n/250\ AgNO_3 - Ag$$

gave by potentiometer measurement an E.M.F. of 0.13 volt, the silver in the *stronger* solution being at the higher potential, while by Nernst's theory this electrode should have an excess potential of 0.16 volt.

The electrode in the stronger $ZnSO_4$ solution shows a mean excess deflection of 1.07 divisions. A zinc electrode in 2*n* $ZnSO_4$ solution in a glass vessel is therefore about 0.14 volt more negative than a similar zinc electrode in *n*/500 $ZnSO_4$ solution. Borelius observations referred to earlier, gave approximately 0.17 difference in the potentials induced in a conductor upon approaching successively solutions of zinc nitrate containing earthed zinc electrodes when the concentration ratio was 1,000, and the sign of the induced potential indicated that the stronger solution (or the region about it) was more negative. In the opinion of the writer it is not however possible to differentiate in Borelius observations between Volta potentials and the true electrolytic potentials which we are here investigating.

For these observations upon the influence of concentration, it was necessary to keep the electrolyte in the flasks for considerable lengths of time and the possibility of some electrolytic conduction through the glass reduces somewhat the dependence which may be given the results. However, although there is a wide variation in the above small differences, taken as a whole, they indicate that when a single electrode dips in a homogeneous electrolyte containing ions of the metal in a glass vessel, the potential of the metal decreases as the concentration of the solution increases. This is opposite to the theory of Nernst, which has often been approximately substantiated for the quite different cases of *two* electrodes, either both dipping in a non-homogeneous solution, or one dipping in the solution and the other separated from the solution by ionized air.[1]

If from an external source the film on the outside of one flask was raised to a known potential, the other flask and its quadrants being insulated, the deflection was 0.59 of the deflection when this pair of quadrants was earthed. The mean deflection with 4*n* AgNO was

$$2.17 = \frac{2.17}{.59 \times 7.50} = -.49 \text{ volt.}$$

The mean deflection with 2*n* ZnSO = 5.02 = 1.11 volts. Both of these potentials are seen to be in fair agreement with the results of direct measurement.

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[1] Guyot, C. R., 153, 867, 1911.

CONCLUSIONS.

A new method for measuring absolutely single electrode potentials has been developed. The results obtained indicate that the potential of a metal in a homogeneous normal solution of one of its salts is about 0.5 volt more negative than the potential deduced from electrocapillary phenomena and usually found in tables. Increasing the concentration of a salt solution contained in a glass vessel appears to lower the potential of an electrode of the metal of the salt.[1]

The writer wishes to express his indebtedness to Mr. C. G. Cummings for assistance in the preliminary observations.

WORCESTER POLYTECHNIC INSTITUTE,
April 24, 1915.

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[1] After this paper had been sent to the editors, a second paper of Borelius (Ann., 22, p. 927, 1914) came to the writer's attention, in which the experiments described in the earlier paper were repeated with electrolytes contained in paraffin-coated flasks connected with a calomel electrode by a syphon. In contrast to the previous results, these later observations gave values for the potentials outside the glass vessels which were in accord with Nernst's theory. The writer, with the assistance of Mr. A. G. Aldrin, has repeated the concentration observations described above using vessels of various shapes of clean glass, glass vessels covered inside with paraffin, and glass vessels covered with shellac. The results with clean glass have been similar to those described above, *i. e.*, opposite to Nernst's theory. A limited number of observations with coated glass have usually given qualitative agreement with the theory. Further investigation is in progress.

LEAKAGE OF GASES THROUGH QUARTZ TUBES.

By E. C. Mayer.

Historical.

BESIDES the work which has been undertaken on the investigation of the flow of gases through quartz and glass, a considerable amount of attention has been given to the determination of the absorption and diffusion of gases through metals, principally iron, palladium and platinum. Among the most important work on metals may be mentioned that of Lockyer,[1] Travers,[2] Ramsay and Travers,[3] Winkelmann,[4] Graham,[5] Beetz,[6] Hoitsema,[7] Schmidt,[8] Richardson, Nicol, and Parnell,[9] Richardson,[10] and Dorn.[11] The gases investigated included hydrogen, helium, and argon.

That quartz is permeable to gases has been found by Villard,[12] Jaquerod and Perrot,[13] and Richardson and Ditto.[14]

Object.

The purpose of the present investigation was to determine the leakage of hydrogen, nitrogen and oxygen through a quartz tube, and to see whether there existed any relation between the amount of leakage and the pressure and temperature of the gas.

Apparatus.

The apparatus employed is shown in Fig. 1. The manometer consists of the long glass tube *ABCDE* joined to the cylindrical reservoir *GH* by means of black pressure tubing *FG*. *F* is a one-way stopcock. *DE* is inclined to the horizontal in the manner shown so that small differences of pressure are easily detected. A difference of pressure of 1 cm. of the gas under consideration is accompanied by a movement of the mercury in *DE* of 2.99 cm.

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[1] J. N. Lockyer, Proc. Roy. Soc., 1895, vol. 58, p. 193.

[2] M. W. Travers, Proc. Roy. Soc., 1896, vol. 60, p. 449.

[3] Ramsay and Travers, Proc. Roy. Soc., 1897, vol. 61, p. 267.

[4] A. Winkelmann, Ann. d. Physik, 1901, vol. 311, p. 104; 1902, vol. 313, p. 388; 1905, vol. 321, p. 773; 1906, vol. 324, p. 1045.

[5] T. Graham, Pogg. Ann., 1869, vol. 136, p. 317; 1866, vol. 129, p. 580; 1866, vol. 129, p. 602.

[6] W. Beetz, Sitzungsber. der Bayer. Akad., 1878, p. 157.

[7] C. Hoitsema, Zeitschr. f. physik. Chem., 1895, vol. 17, p. 40.

[8] G. N. St. Schmidt, Ann. d. Physik, 1904, vol. 318, p. 747.

[9] Richardson, Nicol, and Parnell, Phil. Mag., 1904, vol. 8, pp. 1–29.

[10] O. W. Richardson, Cambridge Phil. Soc. Proc., 1905, vol. 13, p. 27.

[11] E. Dorn, Phys. Zeitschr., 1906, vol. 7, p. 312.

[12] P. Villard, Comptes Rendus, 1900, vol. 130, p. 1752.

[13] Jaquerod and Perrot, Archives des Sciences, 1904, vol. 18, p. 613; 1905, vol. 20, p. 454.

[14] Richardson and Ditto, Phil. Mag., 1911, vol. 22, p. 704.

The eudiometer consists of a glass tube *JK* calibrated in grams of water correct at 15° C. This is joined to a tube *LM* at *L*. *R* and *N* are one-way stopcocks. *Q* is a mercury reservoir, joined to the eudiometer by means of the black pressure tubing *NP*.

Heating was obtained by means of an electric furnace. Temperature was measured by a Paul unipivot pyrometer. Specimens of Jena glass and quartz were joined to the main apparatus at *S*. The specimen of transparent quartz was 16.5 cm. long, 1.9 cm. internal diameter, 0.05 cm. wall thickness. The Jena glass specimens were of approximately the same dimensions except that they had a wall thickness of 0.18 cm.

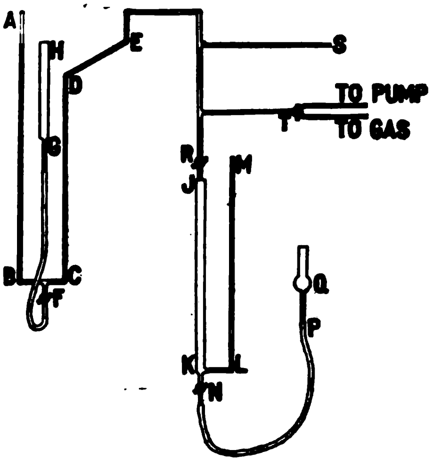

Fig. 1.

PROCEDURE.

The following procedure was adopted when it was desired to take a determination with the gas under atmospheric pressure. Connecting to the pump by means of stopcock *T*, the entire apparatus was exhausted; then turning *T* to the next position, gas was introduced. This was repeated twice so that the apparatus should be well washed with the gas. *R* was then closed and the gas trapped in the eudiometer could be placed under any pressure desirable by raising or lowering *Q*. This entire procedure was done only after the furnace had been maintained steadily at the desired temperature for at least one hour. The gas passed through a calcium chloride drier before entering the apparatus. Cock *T* was now closed. *GH* was raised so that the mercury stood somewhere in the upper part of *AB* and in the lower part of *DE* (at somewhat lower level than mercury in *AB*). *F* was then closed. By referring to a calibration curve, an amount that *GH* should be raised was noted, so that after having raised *GH* this amount, and then opened *F*, mercury in *DE* would rise to same level as mercury in *AB*. If mercury would not rise all the way to this level, *R* was opened until sufficient gas had passed from main apparatus into eudiometer, and mercury in *DE* did come to this level. *R* was then closed. Mercury in *AB*, *GH* and *DE* would then be at the same level, and gas in apparatus would be under atmospheric pressure. Cock *F* was now closed, to remain closed throughout the determination.

The procedure was entirely analogous if the gas was to be under an initial pressure greater or less than one atmosphere.

If gas escaped by absorption or diffusion through the specimen, mercury in *DE* rose. Such movements were read to an accuracy of 0.1 cm. and estimated to 0.01 cm. Readings were reduced to 76 cm. pressure and 15° C.

Theory.

Before discussing the data, it seems desirable to determine what results one may be led to expect from a theoretical consideration of the flow of gas in one direction, assuming an infinite solid (see Fig. 2) with two parallel plane faces whose distance apart is c. It may be shown that a small increment of gas dm flowing through a slab of thickness dx in a time dt is given by

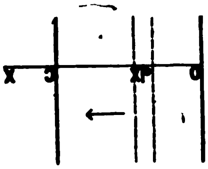

Fig. 2.

$$dm = -a^2 q \frac{\partial u}{\partial x} dt, \tag{1}$$

where q is the cross-section of the slab, $\partial u/\partial x$ the pressure gradient, a^2 the constant of flow. a^2 is the quantity of gas traversing unit area of the slab in unit time when the pressure gradient is unity.

Let the origin be in one face and the axis of X perpendicular thereto. Consider the initial pressure in the solid any function of x and suppose the pressure of the left-hand face of the solid is a constant β, and the right-hand face at zero pressure; we must solve the equation

$$\frac{\partial u}{\partial t} = a^2 \frac{\partial^2 u}{\partial x^2}. \tag{2}$$

We find[1]

$$\mu = \frac{2}{c}\sum_{m=1}^{m=\infty}\left[\epsilon^{-\frac{a^2m^2\pi^2}{c^2}t}\sin\frac{m\pi}{c}x\int_0^c f(x)\sin\frac{m\pi}{c}x\,dx\right] + \beta\left[\frac{c-x}{c} - \frac{2}{\pi}\sum_{m=1}^{m=\infty}\frac{1}{m}\epsilon^{-\frac{a^2m^2\pi^2}{c^2}t}\sin\frac{m\pi x}{c}\right] \tag{3}$$

as our required solution.

Since $u = f(x)$ when $t = 0$, if $u = 0$ when $t = 0$, $f(x) = 0$ when $t = 0$.

Differentiating[2] u with respect to x and integrating[3] with respect to t between the limits $t = 0$ and $t = T$, we obtain

$$M = a^2q\frac{\beta}{c}T - \frac{2\beta qc}{\pi^2}\left[\left(\sum_{m=1}^{m=\infty}\frac{1}{m^2}\epsilon^{-\frac{a^2m^2\pi^2}{c^2}T}\right) - \frac{\pi^2}{6}\right], \tag{4}$$

where M is the total mass of gas which has passed in a time T through the left-hand face of the solid.

If $f(x)$ is not zero when $t = 0$, but if $f(x) = b$, constant, then it may be shown that M becomes

$$M = a^2q\frac{\beta}{c}T - \frac{2\beta qc}{\pi^2}\left[\left(\sum_{m=1}^{m=\infty}\frac{1}{m^2}\epsilon^{-a^2\frac{m^2\pi^2}{c^2}T}\right) - \frac{\pi^2}{6}\right] + \frac{4bqc}{\pi^2}\left[\left(\sum_{m=1}^{m=1,3,5\ldots}\frac{1}{m^2}\epsilon^{-a^2\frac{m^2\pi^2}{c^2}T}\right) - \frac{\pi^2}{8}\right]. \tag{5}$$

If $u = \beta$ when $x = 0$, $u = \gamma$ when $x = c$, and if $u = f(x) = b$, constant, when $t = 0$, M becomes

$$M = a^2q\frac{(\beta-\gamma)}{c}T - \frac{2(\beta-\gamma)}{\pi^2}qc\sum_{m=1}^{m=\infty}\left[\frac{(-1)^m}{m^2}\epsilon^{-a^2\frac{m^2\pi^2}{c^2}T} + \frac{\pi^2}{12}\right] - \frac{4(\beta-b)}{\pi^2}qc\sum_{m=1}^{m=1,3,5\ldots}\left[\frac{1}{m^2}\epsilon^{-a^2\frac{m^2\pi^2}{c^2}T} - \frac{\pi^2}{8}\right]. \tag{6}$$

RESULTS.

In the experiments with Jena glass, there were no indications of leakage. It was impossible to use higher temperatures than 800° C. as the Jena glass became too soft. Also at the higher temperatures it was not feasible to use pressures much lower or higher than one atmosphere because of the softness of the glass. From the results it seems probable that Jena glass is not permeable to the common gases at moderately high temperatures.

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[1] W. E. Byerly, Fourier's Series and Spherical Harmonics, 1893, pp. 38, 105.

[2] Byerly, p. 68. E. Goursat and E. R. Hedrick, Mathematical Analysis, 1904, vol. 1, p. 365. H. S. Carslaw, Fourier's Series and Integrals, 1906, pp. 55, 62.

[3] Goursat and Hedrick, p. 364.

A series of determinations at atmospheric pressure and room temperature were taken to see whether hydrogen or oxygen leak through quartz with the result that no leakage was found.

The results for hydrogen at temperatures 330°, 430°, 550°, and 710° C. are shown by the curves, Figs. 3 to 6. Time in minutes is plotted as abscissas and volume of leakage reduced to 15° C. and 76 cm., in centimeter lengths of the tube *DE* as ordinates. The pressures used were

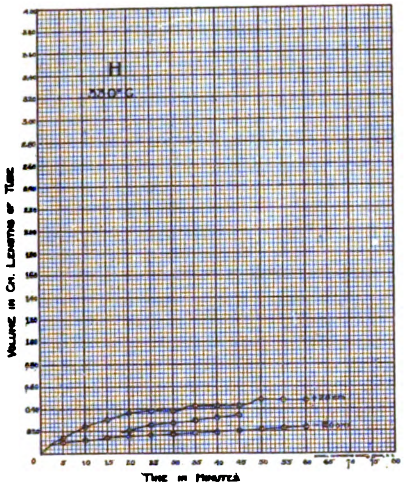

Fig. 3.

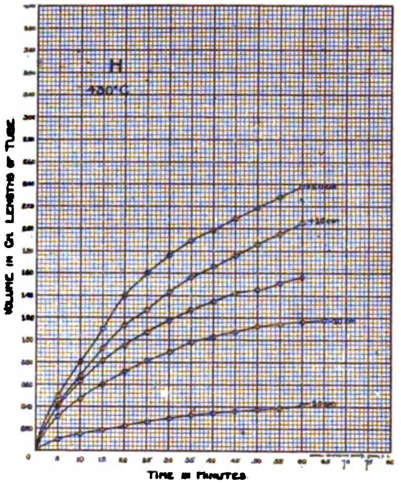

Fig. 4.

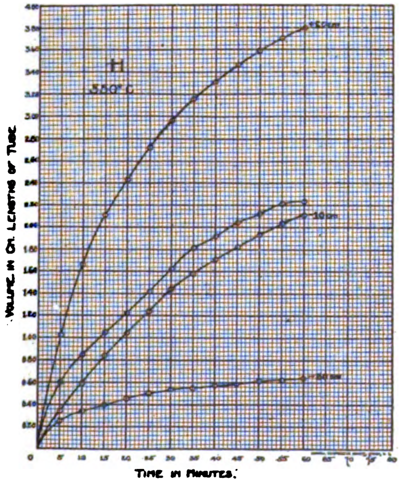

Fig. 5.

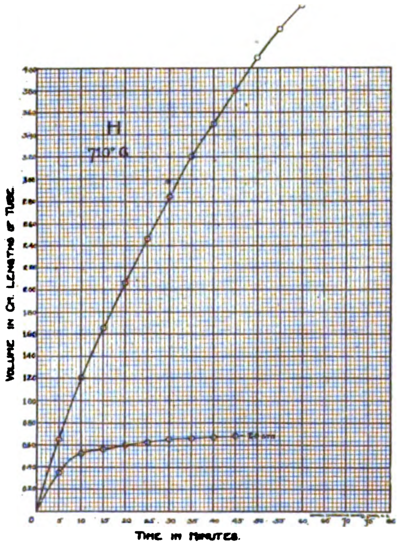

Fig. 6.

20 cm. above atmospheric pressure, 10 cm. above, atmospheric pressure, 10 cm. below, and 20 cm. below. Curves are designated to show under what pressure they were obtained. Determinations were taken for one hour.

One centimeter length of the tube *DE* corresponds to a volume of 0.217 cu. cm.

From an inspection of the curves, it is seen that temperature remaining constant, leakage increases with an increase in pressure. Furthermore it appears that the gas leaks more rapidly at the beginning of a determination than later. With the apparatus in the present work it is impossible to distinguish between the loss of gas by diffusion and by absorption by the walls of the specimen. However it is believed that the loss by absorption had been reduced to a minimum as the specimen was always maintained at the desired temperature for at least one hour before readings were taken, and furthermore the apparatus was washed with the gas twice immediately before the final gas was introduced for experimentation.

If curves are plotted to show the leakage of hydrogen under like conditions of pressure, it will be noted that the leakage increases with temperature, the increase being considerably more marked at the higher pressure.

The results for oxygen at temperatures 280°, 420°, 550° and 690° C. are shown by curves, Figs. 7 to 10.

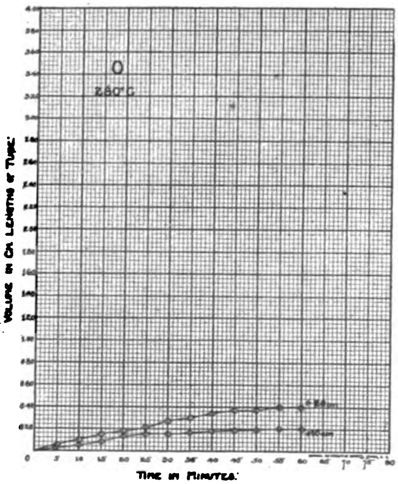

Fig. 7.

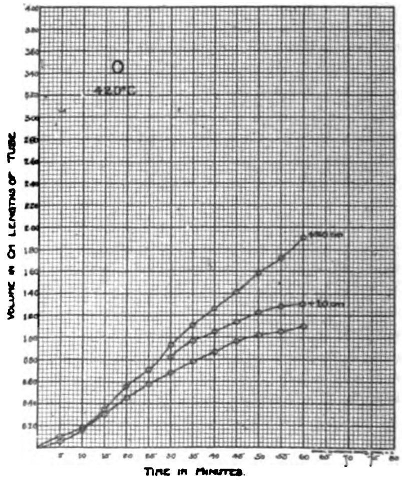

Fig. 8.

Among the curves no data are given corresponding to pressures smaller than one atmosphere. Under these conditions not a single trace of leakage of oxygen was detected.

The data for oxygen, like that for hydrogen, show an increase in leakage with increase in pressure at constant temperature, and a greater leakage with increase in temperature, pressure remaining constant.

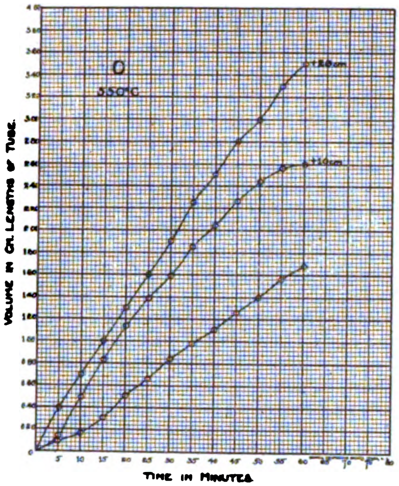

Fig. 9.

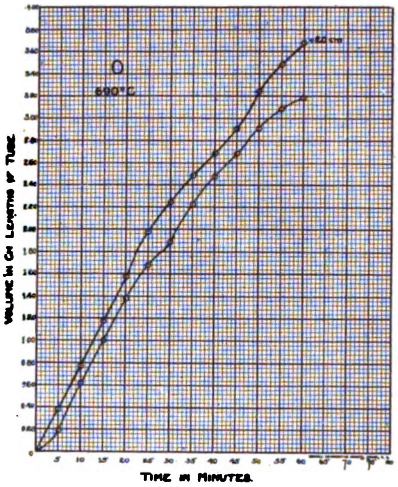

Fig. 10.

The data for nitrogen for temperature 430°, 550° and 700° C. are plotted in Figs. 11 to 13. No leakage of the gas was detected at the

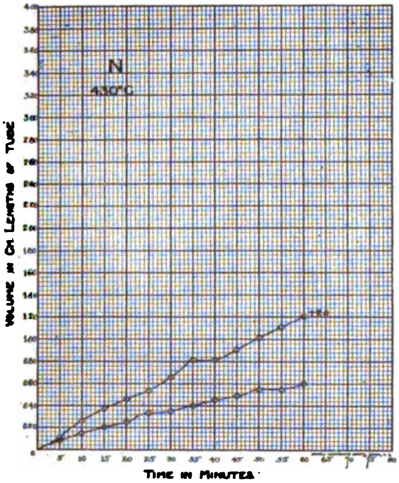

Fig. 11.

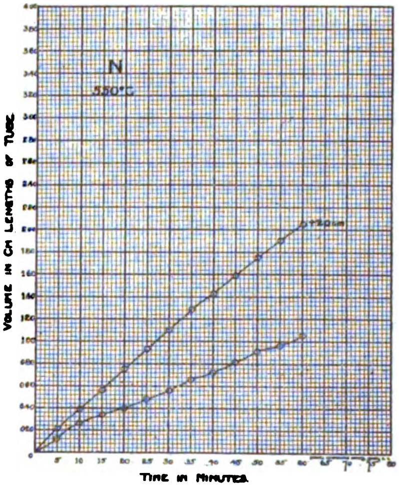

Fig. 12.

lowest temperature of about 300° C. as in the case of hydrogen and oxygen, nor was there any indication of leakage corresponding to a pressure lower than one atmosphere. Here again, at constant temperature, leakage increase with an increase of pressure, and at constant pressure, leakage increases with an increase in temperature.

Curves, of which Fig. 14 is an example, are interesting, as they show the relative leakage of hydrogen, oxygen and nitrogen under like conditions of pressure and approximately like conditions of temperature. In every instance, it is seen that hydrogen leaks most rapidly, and nitrogen least rapidly.

The theoretical treatment outlined above furnishes equations (4), (5) and (6), by means of which it is possible to check the experimental data. In the case of hydrogen leaking into the atmosphere, if $b = 0$, equation (4) may be applied.

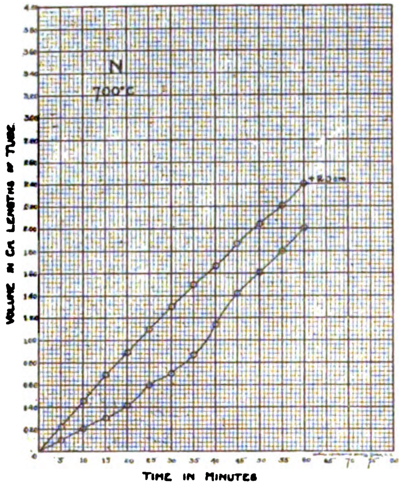

Fig. 13.

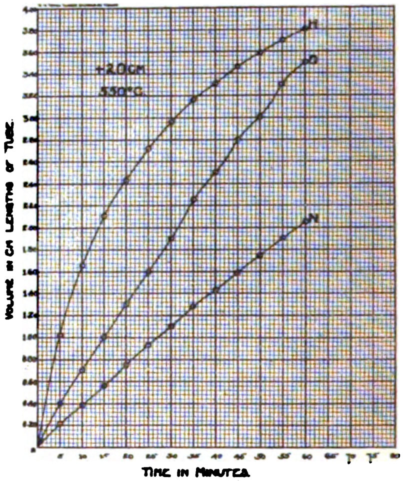

Fig. 14.

By equation (4) and the leakage for hydrogen at one atmosphere, 430° C., and after 60 minutes, an approximate value (0.000003474) of a^2 was computed and this used to calculate data for curves for hydrogen at 430° C. The first four terms only of the infinite series in equation (4) were taken. M was expressed in centimeter lengths of the tube DE (see Fig. 1), q in square centimeters, β in meters of mercury and T in minutes.

A comparison of the curves so determined with those obtained experimentally does not indicate a close agreement, particularly for a pressure 20 centimeters below atmospheric.

If $b = \gamma =$ constant, the curves computed on basis on equations (4) and (6) will be similar.

If b constant (to be determined from data as stated below), and $\gamma = 0$, equation (5) may be applied. Now if curves be drawn showing the relation between the quantity of hydrogen leaking at 430° C. (for example, in equal time), and the pressure, the positive X-intercept indicates that under a pressure represented by this intercept, hydrogen does not leak, irrespective of the time. If b is taken equal to 25 centimeters (the average positive X-intercept) and an approximate value (0.00000917) of a^2 is computed, and curves plotted from calculations by means of equation (5), these curves again do not check with those found experimentally, the largest deviation occurring for a pressure of 56 centimeters.

However it appears hardly probable that hydrogen exerting a definite pressure b exists in the interstices of the quartz as would be assumed by the theory summed up in equation (5). If quartz does contain occluded hydrogen, it seems reasonable to assert that this gas is in equilibrium and forms, as it were, a constituent part of the quartz itself. So that of the two ideas proposed, the one based on equation (4) appears the more likely. Inasmuch as this does not explain the results adequately, we cannot offer any positive explanation of the leakage of hydrogen through quartz. Possibly some other theory may be more applicable. The experimental results for oxygen and nitrogen seem to differ even more widely from the corresponding results obtained by theory.

Summary and Conclusion.

A quartz tube of the transparent variety was found to be pervious to hydrogen at temperatures ranging from 330° C. to 710° C., and at pressures varying from 20 cm. mercury below to 20 cm. mercury above atmospheric pressure. In the case of oxygen and nitrogen, no leakage could be detected for pressures less than one atmosphere. Nitrogen did not seem to escape until a temperature of about 430° C. was obtained. At constant temperature, the results for all gases showed considerable increase in leakage with increasing pressures. Under approximately like conditions, hydrogen leaks most rapidly and nitrogen least rapidly.

The results may possibly be explained by assuming that if the quartz contains occluded gas, that this gas is in equilibrium and forms a constituent part of the quartz itself. It is reasonable to believe that this occluded gas does not effect the process of diffusion in any other manner.

The writer wishes to acknowledge his indebtedness to Prof. J. S. Shearer, at whose suggestion the work was begun, and particularly to Prof. E. G. Merritt, who has aided and encouraged the work in every possible way. Valuable assistance has been received from Dr. R. P. Anderson, Dr. E. H. Kennard and Prof. F. R. Sharpe.

THE GEIGER APPARATUS FOR THE PHOTOGRAPHIC REGISTRATION OF ALPHA AND BETA PARTICLES.

BY J. E. SHRADER.

IN 1908 Rutherford and Geiger[1] devised an electrical method for counting alpha particles given off by radio-active substances. The method may be briefly described as follows: Through a small opening the alpha particles were allowed to enter a strong electric field between a wire and a coaxial cylinder. The entrance of each single particle produced ions, which in this strong electric field gave rise to a current by collision between the wire and the cylinder. The current, thus produced, was detected by a quadrant electrometer, which was connected to the wire while the cylinder was connected to the negative terminal of a high potential battery. The gas in the cylinder was carbon dioxide at reduced pressure.

The difficulty encountered in this experiment was that ionization or "natural disturbance," as the authors call it, arose from the walls of the cylinder, as they explain, and gave a deflection of the electrometer when no alpha particles entered the vessel. By using a cylinder of small diameter and carbon dioxide at reduced pressure they found that these disturbances could be made very small.

In order that a greater number of particles might be counted Rutherford and Geiger[2] devised another form of apparatus to be used with a string electrometer and a photographic registration apparatus.

The ionization chamber was a cylinder 3 cm. long with a hemispherical end. The rays entered the chamber through a small mica window in the hemispherical end. A rod with a spherical knob was insulated in the axis of the cylinder. This rod was connected to a string electrometer which was connected to earth through a high resistance of alcohol and xylol. A high negative potential was applied to the cylinder. The gas used in the chamber was helium at about 20 cm. pressure. This gas greatly decreased the deflections due to "natural disturbances."

Later, Geiger[3] used a fine point inside a cylindrical ionization chamber and was able to get a discharge at atmospheric pressure with a positive potential of about 1,200 volts applied to the cylinder. The cylinder was 2 cm. in diameter and 4 cm. long. The end of the cylinder was closed except for an opening 1.4 mm. in diameter through which the rays entered. The point which was a fine steel needle extended to within .8 cm. of the end. The difficulty encountered was to find a point which was free from "natural disturbances." The choice of a point was made on examination with a microscope. The point was cleaned with alcohol and if it gave "natural disturbances" it was heated in the Bunsen flame. This treatment often removed the difficulty.

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[1] Proc. Roy. Soc. (A), 81, 141, 1908.

[2] Phil. Mag. (6), 24, 618, 1912.

[3] Deut. Phys. Gesell., 15, 534, 1913.

An investigation along the line of Rutherford and Geiger's original experiment was made by Myssowsky and Nesturch.[1] They were not able to secure conditions which were free from "natural disturbances." Their conclusions were that the method was untrustworthy and could not be used to determine with accuracy the number of particles given off by radioactive substances.

At the suggestion of Professor Pegram, of Columbia University, the author began an investigation of the conditions for readily getting the result observed by Geiger.

In these experiments an ionization chamber of the same type as that used by Geiger was employed. Not having a string electrometer at my command, I made a Wilson tilted electrometer, which, with a liquid resistance of alcohol and xylol served the purpose very well. With this arrangement thirty or forty deflections per minute could easily be counted. A diagram of the arrangement is shown in Fig. 1, *a*.

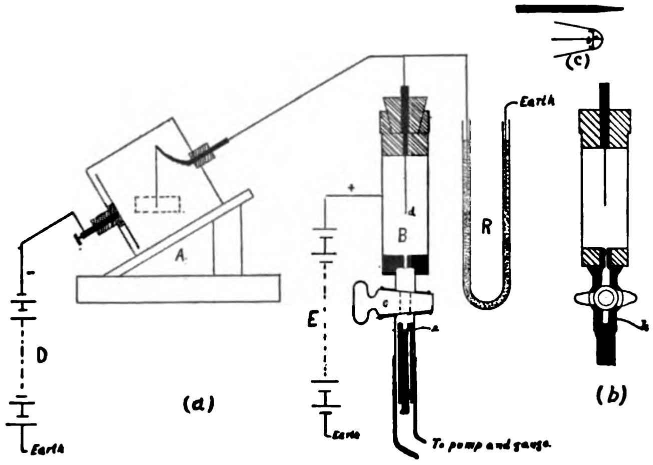

Fig. 1.

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[1] Ann. der Phys., 43, 461, 1914.

Much difficulty was experienced in finding points which were free from "natural disturbances." These "natural disturbances" are shown by a deflection of the gold-leaf of the electrometer when no rays enter. These disturbances may be intermittent or continuous. When they are intermittent they give rise to a sudden deflection of the gold-leaf. This is due to its gaining a charge which immediately leaks off through the high resistance bringing the leaf again to its zero position. If the disturbances are continuous the leaf remains deflected as long as the discharge continues. When a deflection is due to an entering particle the fact can be determined by removing or screening the source of radiation, upon which the leaf will remain quiet. To distinguish the discharge caused by an entering ray from the discharge caused by a "natural disturbance," I will refer to it as the *ray discharge*.

In the preliminary work, long slender needles were used as points. The smoothest and finest points were selected on examination with a microscope. These were carefully cleaned with alcohol and if they gave "natural disturbances" they were carefully heated in the Bunsen flame. Occasionally this would remedy the difficulty. It was observed that best results were obtained by heating just enough to blue the point. If the point was heated until it turned gray it could not be made to give the ray discharge. Careful heating in the oxidizing flame of the blast lamp always gave best results.

Among a number of samples of needles two types of points were found. One type has a rounding slope toward the end, which, as seen through the microscope, seems very blunt. The other kind, called "sharps" by the manufacturer, has two slopes toward the point, the last slope bringing the needle to an extremely sharp point. Most slender needles have the first kind of point. Even among the kind called "sharps," the finer needles do not have better points than those which are coarser.

A dozen of number 9 "sharps" were selected to be tested. Of these, five gave the ray discharge while the others gave only "natural disturbances." The other remaining seven were heated by the blast lamp and five of these were made good, so that only two out of the twelve failed altogether. However none were entirely free from disturbances and these became very numerous if the voltage applied to the cylinder was increased over a short range. These twelve needles were now laid carefully away exposed to the air of the room. Four days later they were again tested under the same conditions. Only one, and this one had been previously heated by the blast lamp, would now give the ray discharge. Four days later they were tested again. The one previously in good order now failed, but two of the others gave the ray discharge. Upon reheating all except one were made good.

From the foregoing results it would appear that the points were continuously undergoing a change in their surfaces. This might be due to collection of dust particles, condensation of water vapor, or the formation of a gas layer. To investigate this point further it seemed desirable to use a platinum point so that it could be heated without destroying the shape of the point or roughening the surface. Accordingly a platinum wire (no. 20, B. & S.) was pointed by grinding on an emery stone and turned true in a jeweler's lathe with a smooth fine-grained stone until it was fairly sharp. The finishing was done by hand on the stone. In this way a good point, even sharper than could be found on the best needles, was made.

All points at first gave natural disturbances. These were now heated in the blast lamp at intervals and tested. The disturbances became less frequent as the heating proceeded and after prolonged heating ceased altogether. Dipping the point while red-hot into nitric acid seemed to help remove the disturbances. Many times when the point gave a good deflection for the ray discharge I have watched for ten minutes at a time without detecting a single disturbance. Occasionally, on standing for some time with no potential applied some disturbances would appear. These disturbances may be due to occlusion of gases, condensation of moisture on the point or the collection of dust particles. The two latter causes seem the more obvious since the introduction of fresh air into the apparatus often results in disturbances. These disturbances, however, disappear upon reheating and dipping into nitric acid.

If a fresh point is heated just enough for the ray discharge to appear it is more sensitive than if heated thoroughly. This sensitiveness gradually decreases until in the course of a half of an hour it is about one sixth of its former value. The change in the sensitiveness now changes more slowly and finally reaches a very small value. When heated thoroughly the sensitiveness of the point remains constant, no change being observed during the greater part of a day.

If, in any circumstance, a spark discharge passed inside the cylinder, the point always developed disturbances. This is undoubtedly due to the deposit of a foreign substance on the point during discharge, though in such a small quantity that it could not be detected by the microscope. Reheating and dipping into nitric acid usually removed the difficulty, though sometimes a repolishing of the point was necessary.

Use of Different Materials as Points.

Various metals were used as points. Among these were, copper, brass, aluminum, silver, iron and 20 k. gold. All of these oxidize on heating. Though many attempts were made to get the ray discharge from these, none were successful except in the case of silver. A successful silver point was always more difficult to obtain than a platinum point so that no further trials were made with the other metals. Undoubtedly the reason a steel needle gave the ray discharge and the pointed iron wire would not was owing to the polish of the surfaces. This would result in unequal oxidation upon heating, in the case of the hand-pointed points.

THE EFFECT OF THE SHARPNESS OF THE POINT.

A sharpening of the point always results in a lowering of the potential to produce a constant deflection for the ray discharge. A well-seasoned platinum point was used. It was first made quite blunt. It was then heated and tested, noting the potential necessary to give a deflection of ten scale divisions in the telescope. The point was gradually made sharper, then it was heated again and tested under the same conditions. The diameter, $b = 2a$, as shown in Fig. 1, c, was measured with a microscope. The results of the variation of the diameter of the point with the potential of the point necessary to give a constant deflection of ten scale divisions are shown in Fig. 2. It can be seen that as the point becomes very sharp the potential drops very rapidly.

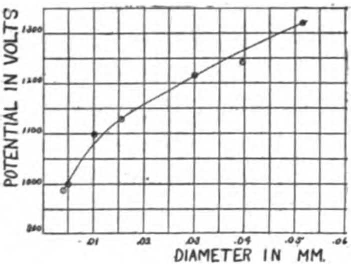

Fig. 2.

THE EFFECT OF THE SIZE OF THE CYLINDER.

In Rutherford and Geiger's original experiment they gave as the cause of the "natural disturbances" the radiations from the sides of the chamber. They found that if a smaller cylinder was used these disturbances became smaller and less frequent. In their second experiment they used helium in the chamber and largely got rid of these disturbances. To test the effect of the size of the cylinder, several cylinders varying in diameter from .9 cm. to 5.3 cm. were made. The result showed that with a thoroughly seasoned point one size of cylinder was as free from disturbances as another. The only difference observed was in the potential to give a ray discharge. In the case of the largest cylinder, the point had to be brought quite close to the end to produce the ray discharge with the potential, 1,400 volts, which I had at my command.

A piece of apparatus similar to that used by Rutherford and Geiger in their original experiment was now made. A small platinum wire was stretched centrally in the axis of the cylinder and fastened to larger brass wires passing through ebonite ends in the cylinder.

While the air was being pumped out an electric current was sent through the wire until it became incandescent. The large brass wires did not extend through to the inside of the chamber so that the extreme ends of the platinum wire which would not be heated to incandescence were not exposed inside the cylinder. When tested before heating the wire, with the chamber partially exhausted, both with the cylinder at positive and then at negative potential, numerous natural disturbances were given off. As the heating proceeded these disturbances became less numerous but could not be removed entirely even though heated for many minutes. The heating was stopped as the wax which secured the ends began to melt. Finally the wire was removed from the cylinder, cleaned and thoroughly heated in the blast lamp and replaced. Now the highest potential (+ 1,400 volts) which I had available failed to show any disturbance or to give the ray discharge though the pressure was reduced to a few millimeters of mercury. This part of the work was not pursued further.

These observations show that the seat of the disturbances is in the point or central wire and that they are not due to the chamber or the contained gas provided it is dry and dust free. This latter will be more fully shown in later observations.

THE EFFECT OF VARIOUS GASES IN THE CYLINDER.

To study the effect of various gases in the chamber the apparatus shown in Fig. 1, *a*, was used. The platinum point was firmly held in the ebonite end by a brass rod. A one-hole rubber stopper slipped over this rod and fitted into the ebonite end. By this arrangement the point was held firmly in place, the chamber was made air-tight and the point could easily be removed. The other end of the cylinder was closed with a metallic end into which was sealed a glass stopcock in which was placed the active rod, *e*. The rays could be cut off by closing the cock. Through the cock the chamber could be exhausted and various gases introduced. Connected to the stopcock was also the pump and pressure gauge.

The gases used were air, oxygen, hydrogen and carbon dioxide. Observations were taken by varying the pressure and observing the potential necessary to give a constant deflection of ten divisions with Alpha rays. The observations were taken with the point at negative and then at positive potential.

Air from the room was at first used. Then the effect of drying it by bubbling it through sulphuric acid and passing it through a calcium chloride tube was observed. Drying the air makes an increase in potential necessary to secure a constant deflection. This is more noticeable at the higher pressures. The introduction of moist air always produced natural disturbances. All other gases were carefully dried. The same point was used throughout these observations. Before a new gas was introduced the point was removed and reheated.

When the pressures were low a small change in potential often resulted in a spark discharge. In this case the point had to be removed and reheated. Many times at the lower pressures disturbances entered which were entirely absent at higher pressures. The number of these were small in comparison to the number of ray discharges so that no attempt was made to get rid of them.

No noticeable difference in the operation of the apparatus was apparent whether the point was negative or positive except that in all cases the potential had to be raised when the point was positive. From the appearance of the curves in Fig. 3 this difference tends to disappear at very low pressures as the curves tend to converge toward the origin. The difference in the negative and the positive potential for the ray discharge for hydrogen is much less marked than for any other gas. The potentials for constant deflection at a certain pressure increases with the density of the gas.

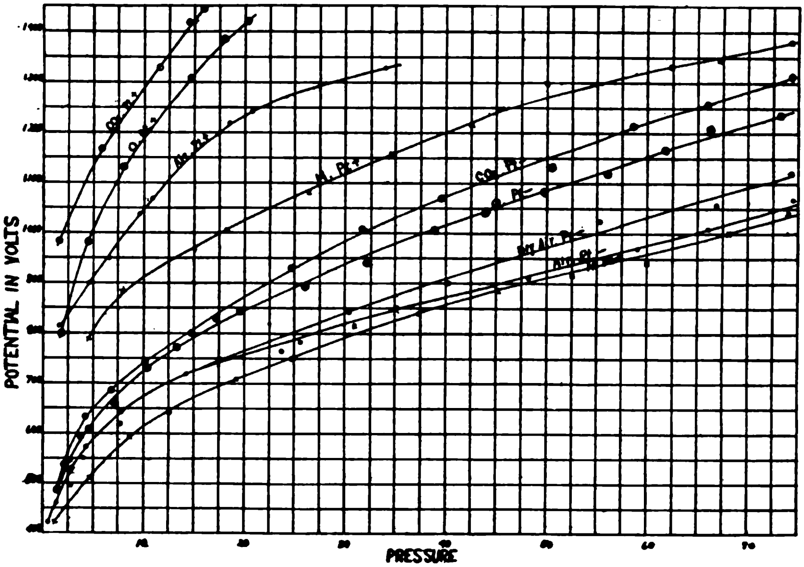

Fig. 3.

THE EFFECT OF GEOMETRICAL DISTRIBUTION OF THE PARTICLES INSIDE THE IONIZATION CHAMBER.

In order that Geiger's method may be effective in determining the number of alpha or beta particles given off by radioactive substances it is quite necessary to know that every particle that enters the chamber is registered. Scattering always occurs when alpha or beta rays penetrate matter or pass through a gas. By scattering in the gas in the cylinder the rays may be distributed at varying distances from the point. The question to be settled is how close to the point must the particle come in order to be registered. To determine this the cylinder previously used, was fitted with a brass end containing several openings 1.4 mm. in diameter distributed at varying distances from the center. These openings were made of larger diameter on the outside so that a brass tube containing a rod made active by exposure at negative potential to thorium emanation could be inserted, the source of radiation being three centimeters from the opening. The distance of the point from the opening was varied from 10 to 25 mm. The active rod was inserted in the openings at various distances from the center of the end. Under these conditions the number of deflections for five minutes was noted. An ebonite end similar to the brass end was now used and similar observations taken. The voltage used throughout was 1,200 volts. The magnitude of deflection did not differ much in the two arrangements when the point was farther from the end. When the point was near the end the deflections were larger with the brass end than with the ebonite end. The results are shown in the following table:

The active rod did not have the same strength in the two cases, so that no comparison can be made as to the number of alpha particles registered by the two arrangements.

These results show that the field from the end of the cylinder to the point is stronger near the center, so that when rays enter to one side, only those that are projected in a favorable direction are registered. If all rays enter this strongest part of the field they are very apt to be registered. If the point should happen to be displaced even a little from the center the rays could not enter the strongest part of the field and would not all be registered. This was tested, and it was found that a small displacement of the point from the center resulted in a diminution of the number of deflections, especially when the point was near the end. With an ebonite end the rays enter a fairly uniform field so that all are more apt to be registered. It is seen that as the point is removed farther from the brass end the number registered is practically the same whether the rays enter at the center or to one side. This last statement is practically

L = length of cylinder; *d* = distance of the point from the end; *r* = the distance from the center of the opening through the particles entered; *N* = number of deflections in five minutes.

Brass End.				Ebonite End.			
L	*d*	*r*	*N*	*L*	*d*	*r*	*N*
4 cm.	25 mm.	0 mm.	37	4 cm.	25 mm.	0 mm.	46
"	"	2	34	"	"	2	44
"	"	3	34	"	"	3	41
"	"	4	25	"	"	4	43
"	"	5	29	"	"	5	45
3.5	20	0	37	3.5	20	0	43
"	"	2	36	"	"	2	43
"	"	5	35	"	"	3	41
				"	"	4	46
3	15	0	37	"	"	5	40
"	"	2	30				
"	"	3	18	3	15	0	45
"	"	4	14	"	"	2	40
"	"	5	3	"	"	3	39
				"	"	5	42
3	10	0	37				
"	"	2	6	3	10	0	46
				"	"	3	40
				"	"	5	38

true in the case of an ebonite end for all distances of the point from the end.

In Geiger's experiment he placed the point 8 mm. from the end. Since this produces a less uniform field, one would not expect to get the same size deflections for all particles, hence at the smaller potentials the smaller discharge would not be shown. That this is true is shown in his table of results; for the potential has to be increased considerably above the voltage at which the ray discharge begins to take place before the number registered becomes constant. With an ebonite end the number registered at all potentials is constant. To show the truth of the last statement some further observations were made, using the chamber shown in Fig. 1, *b*. The point was kept at negative potentials varying from 1,020 to 1,400 volts. Unfortunately I did not have a stronger source of radiation so that a greater number of deflections could be made per minute. In each case the number of deflections in five minutes was observed. The deflection of the electrometer was not quite proportional to the potential to which the leaf was raised, hence the scale of the telescope was calibrated in terms of volts applied to the leaf and the deflections recorded were made numerically equal to the voltage of the leaf. The instrument was made less sensitive for the higher potentials applied to the point. The results are shown in the following table:

Alpha Rays.

Volts.	Deflection.	Number Observed in Five Minutes.
1,020	13	87
1,070	24	85
1,120	35	82
1,180	58	88
1,230	64	87
1,300	86	87
1,340	100	85
1,400	140	81

Beta Rays.

Volts.	Deflection.	Number Observed in Five Minutes.
1,220	18	32
1,280	26	31
1,340	43	31
1,400	62	30

This table shows that the number of particles registered remains practically constant for all voltages. In Fig. 4, curve 1 shows the variation of deflection with voltage. Curve 2 shows this variation for beta rays.

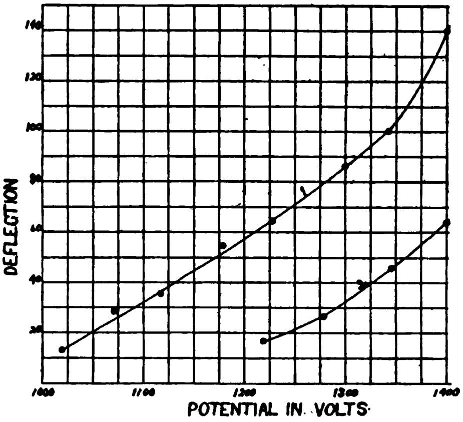

Fig. 4.

The highest potential to which the leaf of the electrometer was raised was 140 volts. This was obtained with 1,400 volts applied to the point. This was the highest potential I had available. Judging from the form of the curve, which is an ionization by collision curve, the application of higher potential might raise the leaf to a potential nearly twice as high before a spark discharge would occur.

USE OF THE APPARATUS FOR DECAY MEASUREMENTS.

The apparatus was now used to determine the rate of decay of thorium B by counting the number of alpha particles given off by its products. The value found was 10.4 hours. Considering the fact that the source of radiation was weak, this is in very good agreement with the accepted value, 10.6 hours.

CONCLUSIONS.

By the use of a platinum point which can be thoroughly heated without destroying the point the "natural disturbances" can all be driven out so that without any difficulty a point can be secured which will give only the ray discharge.

If protected from moist fresh air "natural disturbances" show no tendency to develop during the use of the apparatus.

The seat of the "natural disturbances" is in the point and their number is not affected by the size of the ionization chamber.

At constant pressure, the potential at which the ray discharge occurs is a function of the sharpness of the point.

With a thoroughly heated platinum point, air, hydrogen, oxygen and carbon dioxide, if thoroughly dried, can be used equally well in the cylinder. The only difference is one of the value of the potential necessary to produce the ray discharge.

No more difficulty is experienced in using the point at positive potential than at negative potential. When the point is positive the higher potential is necessary.

With an ebonite end in the ionization chamber quite uniform deflections are obtained for entering rays. As a result, the number of particles registered is constant for all potentials of the point for discharges which give measureable deflections.

The apparatus has been used to determine the rate of decay of thorium B and the agreement with the accepted value is good.

The simplicity of the apparatus and the certainty of the results when a thoroughly heated platinum point is used makes it adaptable to many kinds of radioactive measurements.

WILLIAMS COLLEGE,
May 4, 1915.

A MECHANICAL PROCESS FOR CONSTRUCTING HARMONIC ANALYSIS SCHEDULES FOR WAVES HAVING EVEN AND ODD HARMONICS.

By Hawley O. Taylor.

PERIODIC curves or waves may be analyzed into their constituent harmonics by a variety of methods, some of which make use of mechanical analyzers,[1] some use integration and others measured ordinates.[2] The labor involved when a mechanical analyzer is not at hand is considerable if a complete analysis is desired. Simple methods have been devised for waves which have odd harmonics only, so that schedules for computing the amplitude and phase of the harmonics may be constructed by a mechanical process. The object of this paper is to outline a simple, mechanical process for constructing complete schedules for the analysis of waves containing even, as well as odd, harmonics, and also to point out how a single schedule may be made for any particular harmonic.

Following is the table of symbols which will be used:

$A_1 \cdots A_{n-1}$ = amplitudes of the sine components of first, $\cdots$ $(n - 1)$st harmonics.....cm.
A_k = amplitude of the sine component of the kth harmonic..........cm.
α = time phase..........radians.
B_0 = distance through which axis of periodic curve is removed from coördinate axis....cm.
$B_1, \cdots B_n$ = amplitudes of the cosine components of first, $\cdots$ nth harmonics.........cm.
B_k = amplitude of the cosine component of the kth harmonic..........cm.
C = amplitude of resultant wave..........cm.
k = order of a particular harmonic in a wave..........numeric.
λ = serial number of a particular ordinate or division point on the abscissa of the wave..........numeric.
n = number of parts in a half wave-length..........numeric.
ω = $(2\pi/\tau)$ = angular velocity..........radians/second.
t = time elapsed from a given epoch..........seconds.
t_λ = time elapsed between y_0 and y_λ..........seconds.
τ = periodic time..........seconds.
$u_1, u_2, \cdots$ = sums of pairs of ordinates..........cm.
$v_1, v_2, \cdots$ = differences of pairs of ordinates..........cm.
y = ordinate of periodic wave, or displacement in a wave motion..........cm.
$y_1, y_2, \cdots y_n$ = lengths of the first, second and nth ordinates of periodic curve.........cm.
y_λ = length of a particular ordinate, λ..........cm.

The equation of a periodic curve representing a wave containing harmonics may be written:

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[1] Bibliography 1–9.

[2] Bibliography 10–27.

$$y = \sum_{k=1}^{n-1} A_k \sin k\omega t + B_0 + \sum_{k=1}^{n} B_k \cos k\omega t \tag{1}$$

$$= A_1 \sin \omega t + A_2 \sin 2\omega t + \cdots + B_0 + B_1 \cos \omega t + B_2 \cos 2\omega t + \cdots \tag{2}$$

$$= C_1 \sin (\omega t + \alpha_1) + C_2 \sin (\omega t + \alpha_2) + \cdots + B_0 \tag{3}$$

The analysis consists in finding the coefficients, A and B, there being n of each, making $2n$ unknown quantities to be computed. The A's and B's are then used to find the C's and α's of the final equation, which give the amplitude and phase of each harmonic of the curve.

To compute these coefficients, divide the wave-length, 2π, into $2n$ equal parts from the origin of coördinates on the abscissa, and measure the lengths, $y_1, y_2, \cdots y_{2n}$, of the ordinates erected at the division points.

Take, as an example, the case of $n = 12$. The interval between ordinates is $2\pi/2n = 360°/24 = 15°$.

The values of the 24 ordinates (each with its proper algebraic sign) are arranged in the following scheme and the sums and differences taken:

		y_1	y_2	y_3	y_4	y_5	y_6	y_7	y_8	y_9	y_{10}	y_{11}	y_{12}
	y_{24}	y_{23}	y_{22}	y_{21}	y_{20}	y_{19}	y_{18}	y_{17}	y_{16}	y_{15}	y_{14}	y_{13}	
Sums,	u_0	u_1	u_2	u_3	u_4	u_5	u_6	u_7	u_8	u_9	u_{10}	u_{11}	u_{12}
Differences,		v_1	v_2	v_3	v_4	v_5	v_6	v_7	v_8	v_9	v_{10}	v_{11}	

where

$$u_0 = y_{24}, \qquad u_{12} = y_{12}, \qquad u_{11} = y_{11} + y_{13}, \qquad v_1 = y_1 - y_{23}.$$

A schedule of the v's is made for computing the values of the A-coefficients by placing, in a column at the left, the sines of the angular distances of the ordinates from the origin and putting in the v's as shown below:

In the same way, for computing the B-coefficients, the u's are placed according to the following schedule:

To compute the A's and B's, the numbers represented by the u's and v's are multiplied by the sine of the angle at the left, and the sum of each group taken. This sum is equal to the quantity ($12A_1$ etc.) below each group. From the equations thus established, the coefficients are found. The calculation is shown by the following example:

$$12A_3 = (v_4 + v_8) \sin 0° + (v_1 + v_3 - v_5 - v_7 + v_9 + v_{11}) \sin 45° + (v_2 - v_6 + v_{10}) \sin 90°.$$

B_0 is found from the relation:

$$24B_0 = u_0 + u_1 + u_2 + u_3 + u_4 + u_5 + u_6 + u_7 + u_8 + u_9 + u_{10} + u_{11} + u_{12}.$$

Schedules for A-coefficients.

sin 0		$+v_6$	$+v_4 \quad +v_8$
15	v_1+v_{11}		
30	v_2+v_{10}	$v_1+v_5-v_7-v_{11}$	
45	v_3+v_9		$v_1+v_3-v_5-v_7+v_9+v_{11}$
60	v_4+v_8	$v_2+v_4-v_8-v_{10}$	
75	v_5+v_7		
90	v_6	$v_3 \quad -v_9$	$v_2 \quad -v_6 \quad +v_{10}$
	$12A_1$	$12A_2$	$12A_3$

sin 0	$v_3 \quad +v_6 \quad +v_9$		$v_2+v_4+v_6+v_8+v_{10}$
15		v_5+v_7	
30		v_2+v_{10}	
45		$-v_3-v_9$	
60	$v_1+v_2-v_4-v_5+v_7+v_8-v_{10}-v_{11}$	$-v_4-v_8$	
75		v_1+v_{11}	
90		v_6	$v_1-v_3+v_5-v_7+v_9-v_{11}$
	$12A_4$	$12A_5$	$12A_6$

sin 0		$v_3 \quad +v_6 \quad +v_9$	$v_4 \quad +v_8$
15	v_5+v_7		
30	$-v_2-v_{10}$		
45	$-v_3-v_9$		$v_1+v_3-v_5-v_7+v_9+v_{11}$
60	v_4+v_8	$v_1-v_2+v_4-v_5+v_7-v_8+v_{10}-v_{11}$	
75	v_1+v_{11}		
90	$-v_6$		$-v_2 \quad -v_6 \quad -v_{10}$
	$12A_7$	$12A_8$	$12A_9$

sin 0	v_6		
15		v_1+v_{11}	
30	$v_1+v_5-v_7-v_{11}$	$-v_2-v_{10}$	
45		v_3+v_9	
60	$-v_2-v_4+v_8+v_{10}$	$-v_4-v_8$	
75		v_5+v_7	
90	$v_3 \quad -v_9$	$-v_6$	
	$12A_{10}$	$12A_{11}$	

For checks, we have but to remember that, for $t = 0$, $y = y_0$ or y_{2n}, for $t = \tau/4$, $y = y_{n/2}$, for $t = \tau/2$, $y = y_n$ and for $t = 3\tau/4$, $y = y_{3n/2}$.

Putting these values of t into equation (2), we have:

$$y_{2n} = B_0 + B_1 + B_2 + \cdots + B_n,$$

$$y_n = B_0 - B_1 + B_2 - \cdots + B_n,$$

$$y_{n/2} = A_1 - A_3 + A_5 - \cdots - A_{n-1} + B_0 - B_2 + B_4 - \cdots + B_n,$$

$$y_{3n/2} = -A_1 + A_3 - A_5 + \cdots + A_{n-1} + B_0 - B_2 + B_4 - \cdots - B_n.$$

For the case of $n = 12$, the checks are, therefore:

$$y_{24} = u_0 = B_0 + B_1 + B_2 + B_3 + B_4 + B_5 + B_6 + B_7 + B_8 + B_9 + B_{10} + B_{11} + B_{12},$$

$$y_{12} = u_{12} = B_0 - B_1 + B_2 - B_3 + B_4 - B_5 + B_6 - B_7 + B_8 - B_9 + B_{10} - B_{11} + B_{12},$$

Schedules for B-coefficients.

sin 0	u_6	$u_3 + u_9$	$u_2 + u_6 + u_{10}$
15	$u_5 - u_7$		
30	$u_4 - u_8$	$u_2 - u_4 - u_8 + u_{10}$	
45	$u_3 - u_9$		$u_1 - u_3 - u_5 + u_7 + u_9 - u_{11}$
60	$u_2 - u_{10}$	$u_1 - u_5 - u_7 + u_{11}$	
75	$u_1 - u_{11}$		
90	$u_0 - u_{12}$	$u_0 - u_6 + u_{12}$	$u_0 - u_4 + u_8 - u_{12}$
	$12B_1$	$12B_2$	$12B_3$

sin 0		u_6	$u_1+u_3+u_5+u_7+u_9+u_{11}$
15		$u_1 - u_{11}$	
30	$u_1-u_2-u_4+u_5+u_7-u_8-u_{10}+u_{11}$	$u_4 - u_8$	
45		$- u_3 + u_9$	
60		$- u_2 + u_{10}$	
75		$u_5 - u_7$	
90	$u_0 - u_3 + u_6 - u_9 + u_{12}$	$u_0 - u_{12}$	$u_0-u_2+u_4-u_6+u_8-u_{10}+u_{12}$
	$12B_4$	$12B_5$	$12B_6$

sin 0	u_6		$u_2 + u_6 + u_{10}$
15	$- u_1 + u_{11}$		
30	$u_4 - u_8$	$-u_1-u_2-u_4-u_5-u_7-u_8-u_{10}-u_{11}$	
45	$u_3 - u_9$		$-u_1+u_3+u_5-u_7-u_9+u_{11}$
60	$- u_2 + u_{10}$		
75	$- u_5 + u_7$		
90	$u_0 - u_{12}$	$u_0 + u_3 + u_6 + u_9 + u_{12}$	$u_0 - u_4 + u_8 - u_{12}$
	$12B_7$	$12B_8$	$12B_9$

sin 0	$+ u_3 + u_9$.	u_6	
15		$- u_5 + u_7$	
30	$u_2 - u_4 - u_8 + u_{10}$	$u_4 - u_8$	
45		$- u_3 + u_9$	
60	$- u_1 + u_5 + u_7 - u_{11}$	$u_2 - u_{10}$	
75		$- u_1 + u_{11}$	
90	$u_0 - u_6 + u_{12}$	$u_0 - u_{12}$	
	$12B_{10}$	$12B_{11}$	

$$y_6 = A_1 - A_3 + A_5 - A_7 + A_9 - A_{11} + B_0 - B_2 + B_4 - B_6 + B_8 - B_{10} + B_{12},$$

$$y_{18} = - A_1 + A_3 - A_5 + A_7 - A_9 + A_{11} + B_0 - B_2 + B_4 - B_6 + B_8 - B_{10} + B_{12}.$$

A_1 and B_1 are the amplitudes of the sine and cosine components of the fundamental or harmonic of the first order. The amplitude and phase of this first harmonic are found by combining these two component waves into one wave, given by

$$y = C_1 \sin (\omega t + \alpha_1),^1$$

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[1] Bibliography 29.

having an amplitude

$$C_1 = \sqrt{A_1^2 + B_1^2},$$

and a phase displacement

$$\alpha_1 = \tan^{-1} (B_1/A_1).$$

The amplitude and phase of all other harmonics are found in the same way, but, in plotting the curves, the phase displacement, α, must be measured to the scale of the wave-length of the particular harmonic; *i. e.*, in the case of the third harmonic, say; the phase displacement is represented by a distance one third as long as that which gives it for the first harmonic, etc. In general, for the kth harmonic,

$$y = C_k \sin (k\omega t + \alpha_k),$$

where

$$C_k = \sqrt{A_k^2 + B_k^2},$$

and

$$\alpha_k = \tan^{-1} (B_k/A_k),$$

and for plotting

$$\text{length } \alpha_k = (1/k) \tan^{-1} (B_k/A_k),$$

the scale of the fundamental being used for all harmonics.

C may be taken as always positive and α given the sign of B. Then $+ \alpha$ is measured in the negative direction from the point taken as the origin of coördinates for all of the curves, and $- \alpha$ is measured in the positive direction. The value of α found is always 90° or less, but α is less than 90° only when A is positive, and is greater than 90° when A is negative, or

$$\text{for } + A, \qquad \alpha < 90^\circ$$

and

$$\text{for } - A, \qquad \alpha > 90^\circ \ (= 180^\circ - \alpha).$$

In dividing the abscissa into $2n$ parts for analysis, the origin of coördinates may, of course, be taken at any point along the wave. C_k and the relative phase displacement of the different harmonics are unaffected by the position chosen, but the numerical value of α_k depends upon the location of this point.

A glance at the schedules for A and B reveals a simple, mechanical process by which they may be constructed.

Mechanical Process for Construction of Schedules.

The smaller the number of parts into which the wave-length is divided, the simpler will be the work, but, for accuracy, n should be chosen larger than the highest significant harmonic present. If the presence of the 11th harmonic is suspected, then let $n = 12$ (or any larger number which will divide evenly into 360). For the angular interval between ordinates, divide the wave-length, 360°, by $2n$ (in this case, 24); thus, $360°/24 = 15°$. The sines of these angular intervals are marked in consecutive order in a column at the left, beginning with sin 0° and ending with sin 90°.

The values of the u's and v's are found from the sums and differences of the measured ordinates (y_1, y_2, etc.) according to the scheme already given. (In this scheme, the ordinates for the first half wave-length are placed from left to right on the upper line and for the second half, from right to left on the lower line, the lower line being shifted one place to the left, as shown.)

For A_k, the v's are placed in consecutive order, *down and up*, etc., in each kth space beginning with the kth space below sin 0° and changing sign each time of passing through sin 0°. The subscripts of the v's are from 1 to 11, $[11 = (n - 1)]$, inclusive.

For B_k, the u's are placed in consecutive order, *up and down*, etc., in each kth space beginning with sin 90°, where u_0 is placed, and changing sign each time of passing through sin 0°. The subscripts of the u's are from 0 to 12, $(12 = n)$, inclusive. The sign of both u and v is positive at the beginning.

This process may be illustrated for the ninth harmonic, say, by letting $k = 9$. Then, for the A-schedule, count 9 *down and up*, beginning with *one* at sin 15°; *two* will be at sin 30°, *six* at sin 90°, *seven* at sin 75° and *nine* at sin 45° where $+v_1$ is placed; then, for the second 9, we have *one* at sin 30°, *three* at sin 0° where the sign changes from + to −, and *nine* at sin 90° where $-v_2$ is placed; etc. The count is continued until $+v_{11}$ is written down.

For the B-schedule, begin at sin 90°, where $+u_0$ is placed; then count *one* at sin 75°, *six* at sin 0° where the sign changes from + to −, and *nine* at sin 45° where $-u_1$ is placed; the count is then continued and the u's placed in the same manner as described for the v's until $-u_{12}$ is written down.

Below the group for the A-coefficient is written $12A_9$ and for the B-coefficient, $12B_9$. This completes the schedules. For the general case, nA_k and nB_k are written below each group.

The illustration given also explains how a single schedule is made for any particular harmonic. The harmonic for which a schedule is made may be of much lower order than the highest significant harmonic present in the wave but n should be chosen larger than this highest harmonic, as already pointed out.

Mathematical Discussion.

The opening paragraphs of this discussion are a translation of the comprehensive treatment given in Orlich's book.[1]

"In general, a periodic curve is represented only by a Fourier's series of an infinitely large number of terms, but in most practical cases the terms of higher order are so small that they may be neglected. We may assume that the curve may be represented with sufficient accuracy by a series of $2n$ coefficients, and may let

$$y = \sum_{k=1}^{n-1} A_k \sin k\omega t + B_0 + \sum_{k=1}^{n} B_k \cos k\omega t. \tag{1}$$

"In order to find the coefficients, A and B, we divide the period, τ, into $2n$ parts from the origin of coördinates on the abscissa, and measure the lengths, $y_1, y_2, \cdots, y_{2n}$, of the ordinates erected at the division points. Moreover, the ordinate, y_λ, belongs to the abscissa, t_λ $(= \lambda\tau/2n)$. These corresponding values, y_λ and t_λ, must satisfy equation (1), *i. e.*,

$$y_\lambda = \sum_{k=1}^{n-1} A_k \sin k\omega t_\lambda + B_0 + \sum_{k=1}^{n} B_k \cos k\omega t_\lambda$$

for $\lambda = 1, 2, \cdots 2n$.

"There are $2n$ linear equations from which the $2n$ unknowns, $A_1, \cdots A_{n-1}, B_0, B_1, \cdots B_n$, may be calculated. The calculation gives the result:

$$\left.\begin{aligned} nA_k &= \sum_{\lambda=1}^{2n} y_\lambda \sin k\omega t_\lambda \qquad (4)\\ nB_k &= \sum_{\lambda=1}^{2n} y_\lambda \cos k\omega t_\lambda \qquad (5)\end{aligned}\right\} \text{for } k = 1, 2, \cdots (n-1).$$

For $k = 0$ and $k = n$, the two sums will equal, respectively, $2nB_0$ and $2nB_n$. There is also the relation:

$$k\omega t_\lambda = (2k\pi/\tau)(\lambda\tau/2n) = k\lambda\pi/n. \tag{6}$$

"The correctness of the formulæ, (4) and (5), is established as soon as we allow the number, $2n$, of division points on the abscissa to become infinitely large.[2] Thereby, the infinite summations go over into the integral formulæ:

$$\left.\begin{aligned} A_k &= (2/\tau)\int_0^\tau y \sin k\omega t dt\\ B_k &= (2/\tau)\int_0^\tau y \cos k\omega t dt\end{aligned}\right\} \text{for } k = 1, 2, 3, \cdots.\text{"}$$

These formulæ are the well-known expressions for the coefficients in the Fourier's series.

In order that convenient schedules may be made for use in the analysis of waves which include both odd and even harmonics, a simplification may be affected by combining terms which are removed an equal distance on each side of the middle ordinate $(\lambda = n)$. The expressions for two such ordinates, except for the sign of the sine-term, are equal, as seen from the following:

$$\begin{aligned} \sin k\omega t_{2n-\lambda} &= \sin [\{k(2n - \lambda)\pi\}/n] = \sin [2k\pi - k\pi\lambda/n]\\ &= \sin 2k\pi \cos (k\lambda\pi/n) - \cos 2k\pi \sin (k\lambda\pi/n)\\ &= - \sin (k\lambda\pi/n)\\ &= - \sin k\omega t_\lambda,\end{aligned}$$

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[1] Bibliography 9.

[2] Bibliography 28.

$$\begin{aligned}\cos k\omega t_{2n-\lambda} &= \cos [\{k(2n-\lambda)\pi\}/n] = \cos [2k\pi - k\lambda\pi/n] \\ &= \cos 2k\pi \cos (k\lambda\pi/n) + \sin 2k\pi \sin (k\lambda\pi/n) \\ &= \cos (k\lambda\pi/n) \\ &= \cos k\omega t_\lambda.\end{aligned}$$

Combining these results with equations (4) and (5), we have:

$$nA_k = \sum_{\lambda=1}^{2n} y_\lambda \sin k\omega t_\lambda = \sum_{\lambda=1}^{n-1} (y_\lambda - y_{2n-\lambda}) \sin (k\lambda\pi/n), \tag{7}$$

$$\begin{aligned}nB_k = \sum_{\lambda=1}^{2n} y_\lambda \cos k\omega t_\lambda &= \sum_{\lambda=1}^{n-1} (y_\lambda + y_{2n-\lambda}) \cos (k\lambda\pi/n) \\ &\quad + y_{2n} + y_n \cos k\pi.\end{aligned} \tag{8}$$

The last two terms in (8) correspond to $\lambda = n$ and $\lambda = 0$ or $2n$, which are not included elsewhere in the summations. They are found by putting $\lambda = n$ and $\lambda = 2n$ in (4) and (5).

The construction of schedules from formulæ (7) and (8) follows:

For the case of $n = 12$, the interval between the ordinates, $2\pi/2n$, is 15°. The values of the 24 ordinates are written in two lines as in the scheme given above and the sums, u, and the differences, v, taken as called for in (7) and (8).

Substituting the u's and v's in equations (7) and (8):

$$\begin{aligned}nA_k = {} & v_1 \sin 15k + v_2 \sin 30k + v_3 \sin 45k + v_4 \sin 60k + v_5 \sin 75k \\ & + v_6 \sin 90k + v_7 \sin 105k + v_8 \sin 120k + v_9 \sin 135k \\ & + v_{10} \sin 150k + v_{11} \sin 165k. \\ nB_k = {} & u_0 + u_1 \cos 15k + u_2 \cos 30k + u_3 \cos 45k + u_4 \cos 60k \\ & + u_5 \cos 75k + u_6 \cos 90k + u_7 \cos 105k + u_8 \cos 120k \\ & + u_9 \cos 135k + u_{10} \cos 150k + u_{11} \cos 165k + u_{12} \cos 180k.\end{aligned}$$

By transforming all the angle functions into sines of angles lying between 0° and 90°, and arranging in a column according to angle, the schedules already given are obtained. Each line is multiplied by the sine of the angle set down in the left-hand column. The summations of the groups containing v are, in each case, equal to nA_k, k being the order of the respective harmonic, and of those containing u, nB_k.

$B_0 = (1/2n) \sum_{\lambda=1}^{2n} y_\lambda$, from which the value of B_0 already given is obtained. If the y's are not measured from the axis of the curve, but from a line parallel to it and a distance B_0 from it, the schedules for A and B may still be applied as they stand, for, in that case, each y is changed by an amount equal to B_0, and the way in which the + and − signs are distributed among the y's for each coefficient, causes the B_0 to cancel out in the summations.

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July 2, 1915.

Bibliography.

1. Thomson, Sir Wm., Proc. Roy. Soc., XXIV., p. 262, 1876.
2. Henrici, O., Phil. Mag., July, 1894.
3. Yule, Geo., Phil. Mag., April, 1895.
4. Michelson and Stratton, Am. Jour. Sc., 5, 1898.
5. Le Conte, Phys. Rev., 7, p. 27, 1898.
6. Terada, Zeit. f. Instrument., 25, p. 285, 1905.
7. Rowe, Geo. H., Elect. World, March, 1905.
8. Chubb, L. W., Elect. Jour., Feb. and May, 1914.
9. Orlich, E., "Aufnahme und Analyse von Wechselstromkurven." (Mechanical, Integral and Arithmetical Methods.)
10. Thomson, Sir Wm., Proc. Roy. Soc., XXVII., p. 371, 1898.
11. Fleming, J. A., Lond. Elect., Jan. 22–9, 1892.
12. Perry, J., Lond. Elect., Feb. 5, 1892, and June 28, 1895.
13. Berson, S., Ecl. Electrique, 15, 1898.
14. Houston and Kennelly, Elect. World, XXXI., 1898.
15. Langsdorf, A. S., Phys. Rev., XII., p. 184, 1901.
16. Fischer-Hinnen, Elektrotech. Zeit., May 9, 1901.
17. Kintner, S. M., Elect. World, XLIII., p. 1203, 1904.
18. Harrison, J., Engineering, p. 201, Feb., 1906.
19. Lincoln, P. M., Elect. Jour., V., p. 386, 1908.
20. Pierce, C. A., Elect. World, p. 916, 1911.
21. Grover, F. W., Bull. of Bur. of Stand., p. 567, Dec. 15, 1913.
22. Runge, C., Thesis, "Rechnungsformular zur Zerlegung einer empirisch gegebenen periodischen Funktion in Sinuswellen." 1913.
23. Runge, C., Zeit. f. Math. und Phys., XLVIII., p. 443, 1903.
24. Thompson, S. P., Proc. Lond. Phys. Soc., XIX., p. 443 (discussion of Runge's grouping).
25. Tuttle, E. B., Iowa Engr., Sept., 1906 (discussion of Runge's grouping).
26. Bedell, F., Direct and Alternating Current Manual, Ch. XI.
27. City and Guilds of London Institute (Har. Analys. Sched.).
28. Byerly, W. E., "Fourier's Series and Spherical Harmonics," p. 36.
29. Cohen, A., "Differential Equations," p. 95 (footnote).

THE CHANGE IN THE ELASTICITY OF ALUMINUM WIRE WITH CURRENT AND EXTERNAL HEATING.

BY H. L. DODGE.

THIS paper is the third of a series upon the effect of temperature on the elasticity of wires and deals with aluminum. The apparatus is the same as that used in work with copper and mild steel wires already described in the PHYSICAL REVIEW.[1] Upon these metals very exhaustive tests were made, the necessity of this being evident from the great variation in the results that had been reported. The treatment of the specimens of aluminum and the methods employed to secure a wide variation in the conditions have been the same as are fully described in former papers. In general the results have been the same. Consequently this paper is restricted to a brief discussion of the effects peculiar to aluminum and to a discussion of certain general conclusions regarding the effect of temperature on the elasticity of metals.

The tests have been made upon two samples of aluminum wire known commercially as "soft" and "hard." The former is annealed wire and bends easily, the latter is unannealed and is stronger and stiffer. The wires and their chemical analyses were secured through the kindness of Mr. H. M. Hall, superintendent of the United States Aluminum Co., Massena, N. Y. Below are tabulated the analyses, certain physical constants and data regarding the tests.

Chemical Analyses and Constants.

	Soft Aluminum.	Hard Aluminum.
Iron	.44 per cent.	.32 per cent.
Silicon	.24 " "	.22 " "
Copper	.03 " "	.07 " "
Aluminum	99.29 " "	99.39 " "
Diameter	1.24 mm.	1.44 mm.
Breaking load	22. kg.	38. kg.
Coefficient of expansion	.000025	.000025
Length	57.7 cm.	57.5 cm.
Permanent load	1,114. g.	1,114. g.
Added load	1,048. g.	1,048. g.
Total load per sq. mm.	1.8 kg.	1.3 kg.
Maximum current	23. amp.	
Maximum current per sq. mm.	19.1 amp.	

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[1] PHYS. REV., N. S., Vol. 2, 431, 1913; Vol. 5, 373, 1915.

Aluminum will not stand very heavy loads. The percentage accuracy of the determinations of Young's modulus is consequently not as high as has been the case when the loading and resulting total stretch were considerably greater. The curves may however be regarded as giving the change in the modulus to an accuracy of one per cent. The error in the measurement of the temperature is of course greatest at high temperatures but probably does not exceed ten or at the most fifteen degrees.

Tests upon Soft Aluminum Wire.

The specimen of soft aluminum wire was first subjected to loads of two and four kilograms and a temperature of about 250° C. This treatment straightened out the kinks and lengthened the wire several millimeters. The weights were then made of appropriate sizes and two series of readings were taken with external heating. Series 2, Fig. 1, shows how the rate of decrease of the modulus increased rapidly with increase of temperature until it became uniform at about 100° C. The third series was with decreasing temperature and was similar in character. Series 4, Fig. 1, differs only in the manner of heating, an electric current in the wire itself being used.[1]

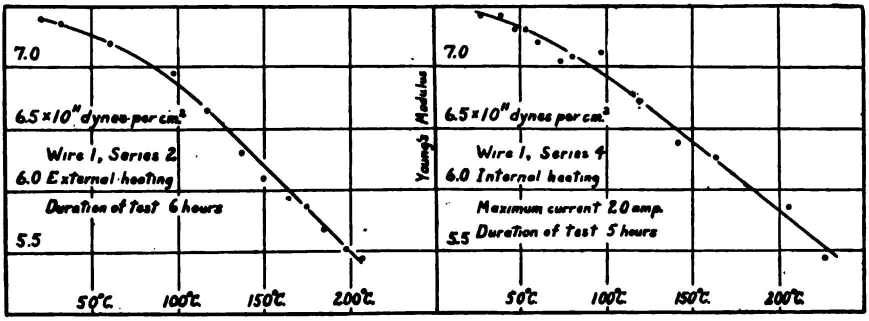

Fig. 1.

Effect of current and external heating upon the Young's modulus of a soft aluminum wire.

A comparison of these results with those shown in series 5, Fig. 2, shows that a permanent change in the properties of the specimen resulted from the treatment in test 4. In this test the temperature reached was higher than before, resulting in some stretching of the wire. The annealing was consequently more thorough. Series 5 was with external heating, increasing and decreasing temperature, and may be regarded as giving the change of Young's modulus with temperature for a thoroughly annealed aluminum wire.

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[1] In all figures dots represent observations with increasing temperature, crosses those with decreasing temperature.

Series 6 was taken in the same manner except that the heating was by a current in the wire itself. The curves in the two drawings are practically the same. They show that a cyclic state had been reached in which Young's modulus becomes a function of temperature and is independent of the manner of heating and the thermal route by which any temperature is reached.

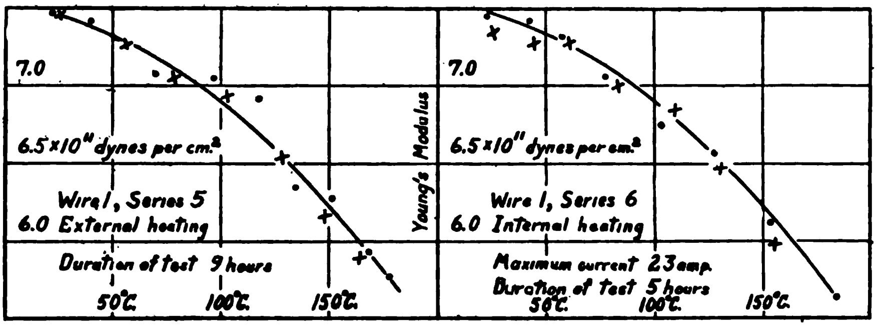

Fig. 2.

Effect of current and external heating upon the Young's modulus of a soft aluminum wire after thorough annealing.

Table I. gives the complete data from which series 6 is plotted. This is characteristic of all the data, except that with external heating a longer time was necessary for temperature equilibrium to be reached.

Tests upon Hard Aluminum Wire.

The sample of hard aluminum wire was carefully straightened and then tested without any preliminary annealing. Series 1, Fig. 3, shows the almost linear relation between the modulus and temperature. This changes slightly with the second heating as shown by the curve of series 2. The next few series of observations were taken under a variety

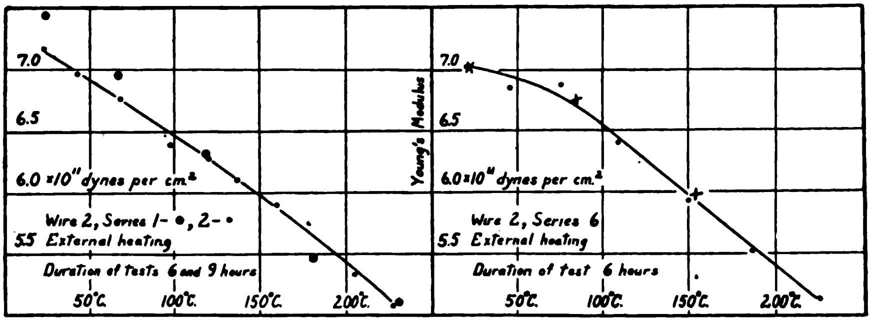

Fig. 3.

Effect of temperature upon the Young's modulus of a hard aluminum wire.

of conditions, some with heavier weights and at higher temperatures. Just before series 6 the wire was heated to about 400° C. This treatment resulted in a partial annealing and produced the change in the properties of the wire shown by Fig. 3. The similarity of these results to those secured with the soft aluminum specimen lead me to believe that further testing with the consequent thorough annealing would have developed the same final conditions as before.

Table I.

Data for Soft Aluminum Wire, Series 6, Internal Heating.

Obs. No.	Time.	Temp.	Stretch.	Current.	No. of Obs.	Young's Modulus $\times 10^{-11}$, Dynes per cm.^{2}
1	9:00 A.M.	22° C.	.0658 mm.	0 amp.	9	74.5
2	10:00	47	.0660	8	10	74.2
3	10:20	57	.0670	11	9	73.1
4	10:35	78	.0694	14	8	70.6
5	10:50	102	.0726	17	10	67.5
6	11:00	128	.0745	19	11	65.8
7	11:15	154	.0800	21	6	61.2
8	11:25	183	.0870	23	23	56.4
9	11:30	156	.0820	21	7	59.8
10	11:40	131	.0758	19	13	64.6
11	11:50	110	.0717	17	10	68.4
12	12:05 P.M.	83	.0700	14	9	70.0
13	1:00	61	.0673	11	9	72.9
14	1:20	44	.0674	8	11	72.8
15	1:45	25	.0668	0	10	73.4

The results of the tests upon samples of soft and hard aluminum wire may be summarized as follows:

1. Aluminum wire can by thorough annealing be brought to a cyclic condition or steady elastic state in which Young's modulus becomes a function of temperature.[1]

2. Within given temperature limits the modulus becomes practically independent of history, the thermal route by which any temperature is reached having no apparent effect on the value of the modulus.

3. Heating by an electric current has no effect other than that caused by the accompanying temperature.

4. The Young's modulus of annealed wire decreases with increase of

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[1] Guthe and Sieg, Phys. Rev., Vol. 30, 610, 1910, and Sieg, Phys. Rev., Vol. 31, 421, 1910, in studying the elastic constants of platinum-iridium wires by means of torsional vibrations found that annealing would bring the wires to such a state that results were easily reproducable.

temperature at an increasing rate. The following table is compiled from the results for thoroughly annealed soft aluminum wire.[1]

TABLE II.

Change of Young's Modulus of a Thoroughly Annealed Aluminum Wire with Increase of Temperature.

Temperature.	Young's Modulus $\times 10^{-11}$, Dynes per $cm.^2$	$\frac{dE \times 10^{-11}}{dT}$	Total Decrease, Per Cent. of E at 20° C.
20° C.	7.50	.0046	0.0
40	7.40	.0057	1.3
60	7.27	.0072	3.1
80	7.10	.0090	5.3
100	6.90	.0112	8.0
120	6.66	.0135	11.2
140	6.38	.0155	14.9
160	6.06	.0165	19.2
180	5.72	.0170	23.8

5. Hard aluminum wire exhibits an almost constant temperature coefficient of elasticity. Annealing does not materially change the value of Young's modulus but it does however affect the rate of change, increasing the temperature coefficient of elasticity for low temperatures and decreasing it for higher values, the dividing temperature being about 100° C.

GENERAL CONCLUSIONS REGARDING THE EFFECT OF TEMPERATURE UPON THE YOUNG'S MODULUS OF METALS.

When the present series of investigations on the effect of current and external heating upon the Young's modulus of metals was undertaken the literature of the subject revealed great inconsistency and lack of uniformity in the results that had been secured. Although most observers had reported a decrease of elasticity with increase of temperature many did not find this to be the case. So great were the variations in the results that no conclusion could be drawn regarding the true nature of the effect of temperature on Young's modulus.

Two explanations were possible. Either every specimen possessed its own peculiar elastic properties or else the apparatus and methods employed were not sufficiently refined for the very delicate measurements required.

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[1] Slotte, Acta. Soc. Scien. Fennicæ, Vol. 26, 1899, for a temperature range of 6° C. to 70° C. reports an almost uniform decrease in the modulus of .16 per cent. per degree. Katzenelsohn, Diss. Berlin, 1887, reports a decrease of .19 per cent. per degree between 0° C. and 100° C.

It was my belief that samples of wire ought by the proper heat treatment to be brought to a condition in which the modulus would be a function of temperature. With this as a criterion the apparatus described in previous papers was developed. The results secured with the cruder forms at once convinced me that a great part at least of the inconsistencies in former work must have been due to poor temperature control and the intrusion of certain factors affecting the accuracy of the determination of the modulus. The greatest difficulties were met when the heating was by an electric current in the wire itself as might have been anticipated from the fact that no satisfactory investigations had ever been carried out with this method of heating.

Copper was chosen for the first tests because of its high electrical conductivity and with the idea that it ought to respond readily to moderate heat treatment. My first paper[1] describes how the copper wire finally reached a cyclic state in which the Young's modulus became a function of temperature, the modulus decreasing at an increasing rate. The experience gained in the study of this metal lead me to believe that there was no reason why other metals should not behave in a similar manner. If any metal were to put this idea to test it seemed as if it would be one possessing such variable and peculiar properties as iron or steel. The second paper[1] describes the results with a mild steel wire. A cyclic state was secured for a temperature range of 20° C. to 475° C. and the general nature of the change of the modulus with temperature proved to be the same as in the case of copper.

Since these experiments were performed almost identical results have been reported by Lea and Crowther[2] with rods of mild steel, nicrocopper, and high-tension brass and by Harrison[3] with nickel wire, although in the latter case anomalous effects occur near the critical temperature. Similar results are also to be found in the work of some of the earlier investigators.

In the present paper aluminum has been shown to yield exactly the same type of results as were secured with copper and mild steel. A considerable amount of data is now available and for the metals that have been mentioned the following generalizations appear to be justified:

1. By thorough annealing the metal can be brought to a cyclic state in which Young's modulus becomes a function of the temperature.

2. The Young's modulus of the metal decreases with increase of temperature, the rate of the change increasing with the temperature.

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[1] *Loc. cit.*

[2] Engineering, Vol. 98, 487, 1914.

[3] Phys. Soc., Proc., Vol. 27, 8, 1914.

3. When the metal is heated by the passage of an electric current the change in the modulus is a pure temperature effect.

In my own mind it seems so reasonable to expect that other metals will behave in the same manner that I am led to predict that these generalizations will be found to be the laws governing the effect of temperature upon the elasticity of metals.[1] Work is being continued in this laboratory with other metals and it is to be hoped that other investigators will continue with different types of apparatus and under different conditions.

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May, 1915.

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[1] Dodge, PHYS. REV., N. S., Vol. 5, 76, 1915.

Second Series. November, 1915 Vol. VI., No. 5.

THE

PHYSICAL REVIEW.

PHYSICAL PHOTOMETRY WITH A THERMOPILE ARTIFICIAL EYE.

By Herbert E. Ives and E. F. Kingsbury.

THE idea of a physical photometer, an instrument to indicate luminous intensities by the position of a pointer, is comparatively old.[1] The feasibility of the idea has been demonstrated, notably by Fery,[2] but it has not heretofore found application in practical form. That this is the case is chiefly because the great field (although not the only one) for the physical photomoter is in the photometry of lights of different color, and this latter is a problem only recently given a satisfactory solution.[3] Put differently, we may say that the physical photometer has had to lie dormant because there has been no way to determine definitely whether a given physical photometer reads correctly.

The present paper describes the development and practical use of an artificial eye, consisting of a sensitive thermopile in conjunction with an absorbing medium whose transmission is a copy of the spectral luminosity curve of the average eye. This artificial eye differs from previous essays in the same direction in the accuracy with which it conforms to the latest determinations of the luminosity curve and in the fact that it has been exhaustively tested for its performance upon test color differences whose photometric values have been established by a satisfactory method of colored light photometry.

Necessary Photometric and Physical Preliminaries.

As a preliminary to the detailed description of the new physical photometer it is desirable to summarize the state of development to which the solution of certain photometric and physical problems must have been brought before physical photometry could be put in practical form.

The Adoption of a Method of Visual Colored Light Photometry.—We may emphasize two features which are practically indispensable in a method of visual colored light photometry if it is to serve as a basis for physical photometry. First, the method must conform to the elementary arithmetical axioms that things equal to the same thing are equal to each other, and that the sum of the separately measured parts shall equal the measurement of the whole. The importance of this is best illustrated by an example of a photometric method which is quite unsuitable, namely, "visual acuity." By this method a monochromatic light measures as more effective than a polychromatic one of the same or greater intensity, as measured by other criteria. Obviously any attempt to develop a physical photometer which shall discriminate between monochromatic and other radiation of the same intensity is beset with extreme difficulty. Second, the visual photometric method should be used only at one definite point in the "condition diagram" determined by brightness and field size. In other words, the infinite number of values which are theoretically possible owing to the existence of the Purkinje and allied phenomena, must be reduced to a single one by the adoption of definite standard conditions of illumination and field size. The practical importance of this restriction lies in the obvious difficulty of constructing a radiometer which shall change its relative spectral sensibility with the intensity of total illumination and with the size of the object presented to its view. This latter restriction is not a serious one although it might at first sight so appear. It is not serious because the study of the photometric problem has shown the disturbing phenomena mentioned to be of importance only at very low illuminations. The adoption of standard high illumination conditions is as necessary to visual colored light photometry as to physical. Deviations from these standard, most useful conditions, are to be met by the use where necessary of correcting "quality factors."

The method of visual colored light photometry to which we have worked in this research is that specified by the use of the flicker photometer, with a photometric field of 2 degrees diameter, under an illumination to give the brightness of a white surface under 25 meter candles, a large enough group of observers being used to form an average eye.

The Establishment by the Visual Photometric Method of a Set of Luminosity Values of Representative Color Differences.—The most important and useful color scale is of course that given by the luminosity curve of the normal equal energy spectrum. With this accurately determined by a photometric method conforming to the arithmetical axioms, the physical photometer problem consists solely in the accurate copying of the curve by the spectral sensibility curve of the radiometer. If the different parts of the spectrum measure correctly then all mixtures of these parts must measure rightly.

The luminosity curve of the equal energy spectrum has been determined by substantially the photometric method outlined by Ives and by Nutting.[4] The curves obtained are shown in Fig. 1 (dashed and dot-and-dashed lines). They are in general similar, but differ somewhat in area and shape of the blue side. These differences will show up as small but detectable differences in the relative values of the complex colors and, pending still more exact determinations of the luminosity curve, the choice of the exact curve to which the physical photometer must conform must be made by a process of trial on other color differences.

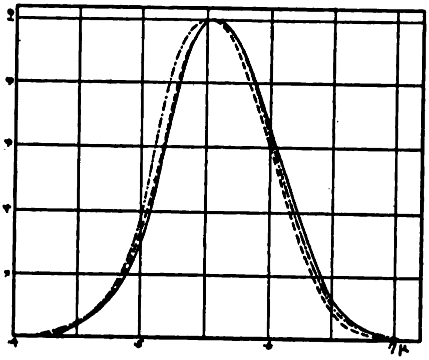

Fig. 1.

Luminosity curves of the equal energy spectrum. Dot and dash line, Ives' data. Dashed line, Nutting's data. Full line, Curve called for to secure agreement between visual and physical photometer values on series of test colors (transmission curve of final luminosity curve solution).

It may be remarked in reference to the spectrum luminosity curve that while its exact determination is all that is necessary to provide a color scale, the practical experimental difficulties, due to the necessity of determining the intensity of the radiant energy through the visible spectrum, are great enough to leave the results so far obtained in some doubt where the greatest accuracy is in question.

The spectral luminosity curve must, therefore, be supplemented by other test colors, whose luminosity values are capable of more exact determination. Such colors are suitable for checking the performance of a luminosity curve solution and for indicating slight changes, but are not suitable for determining it originally. We have had at our disposal for this purpose a series of absorbing solutions, developed for other purposes, whose transmissions have been determined by the standard photometric method by a group of observers representing the average of 61 individuals. These solutions have been described in detail elsewhere. It is only necessary to list them here. They consist of four, as follows:

1. A solution of potassium dichromate in water,
72 grams to one liter solution.
2. A solution of cupric sulphate in water,
53 grams to one liter solution.

These two solutions, placed in one centimeter thick matched glass tanks, should transmit equal amounts of the light from a standard "4-watt" carbon lamp, as determined by the standard visual photometric method. These solutions we have developed[5] and used for the selection of groups of observers whose mean visual characteristics shall be the same as our large group of 61. We shall refer to them here as the "test colors."

3. A yellow solution which in varying concentrations reduces the light from an incandescent solid to visual equivalence with that from incandescent solids at lower temperatures.

Composition.

Cobalt ammonium sulphate	100 g.
Potassium dichromate	.733 g.
Nitric acid (1.05 grav.)	10 c.c.

Mix with distilled water to one liter of solution.

4. A blue solution which in varying concentrations reduces the light from an incandescent solid to visual equivalence with that from incandescent solids at higher temperatures.

Composition.

Nickel ammonium sulphate	50 g.
Ammonia (.90 grav.)	50 c.c.
Ammonium sulphate	10 g.

Mix with distilled water to one liter of solution. Dilute with distilled water containing 10 g. ammonium sulphate per liter.

These solutions[6] we shall refer to as "Fabry solutions," the possibility of the development of such media having been pointed out by Fabry.[7] The transmission of these solutions in thicknesses of one centimeter, at 20° C., against clear water, are accurately given by the equations:

Yellow solution over "4-watt" lamp . . . . $\log_{10} T = -.245\, c^{9}$
Yellow solution over tungsten lamp to reduce to "4-watt" color . . $\log_{10} T = .368\, c^{1.05}$
Blue solution over "4-watt" lamp . . . . $\log_{10} T = -.539\, c^{1.03}$

where "c" (concentration) is expressed in decimal fractions.

The spectral transmissions of these solutions are shown in Fig. 2. It will be seen that solutions 1 and 2 give a comparatively sharp division of the spectrum (of the carbon lamp) into two complementary parts, while the Fabry solutions give a very gradual change of intensity from end to end. We have as well in the yellow solution on the test lamp side, and in the blue solution on the carbon or comparison lamp, side, two means of obtaining the same visual color difference, with slight differences in the spectra.

These solutions give us, therefore, two main different types of color difference, and include the most common type now encountered, namely that between the low and high efficiency incandescent lamps. We have worked upon the assumption that a physical photometer which conforms closely to the determinations of the spectrum luminosity curve and as well measures these color differences accurately is sufficiently practical for immediate needs.

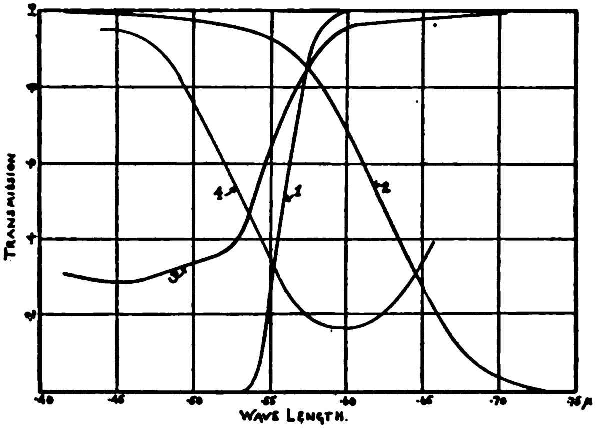

Fig. 2.

Spectral transmissions of colored solutions used to test performance of physical photometer. 1. Yellow test color. 2. Green test color. 3. Fabry yellow solution, 35 per cent. conc. 4. Fabry blue solution, 100 per cent. conc.

The Existence of a Satisfactory, Highly Sensitive Means of Measuring Radiant Energy.—Luminous flux being simply radiant power which has been passed through an evaluating medium, either the retina or a luminosity curve solution, the physical measurement is necessarily one of radiant power measurement. An essential characteristic of the radiometer to be employed is of course that it shall have adequate sensibility to stand the tremendous reduction of intensity which transformation from radiant power to luminous flux involves with our present light sources (a reduction usually of about 99 per cent.). In addition to this the radiometer should give a response directly proportional to the stimulus. Further, its spectral sensibility should be fixed and unchangeable in order that the problem of altering its sensibility to that of the eye shall be capable of definite solution.

In the preliminary study of the problem of physical photometry[1] the chief types of radiometer were studied with reference to the essential characteristics for this purpose. The most sensitive ones (selenium and the photo-electric cell) were found to be deficient in certain essentials and final choice was made of the thermopile, which has of late been subject to considerable study and development.

Practical Details.

The Thermopile and Galvanometer.—The thermopile used in the majority of the work was a linear one of bismuth-silver, Coblentz design, of 18 junctions, having a total resistance of 26 ohms, the junctions being in series. The galvanometer was a d'Arsonval, constructed by Leeds & Northrup. Its period was 6.5 seconds; its internal resistance 12.5 ohms; its critical damping resistance 32.5 ohms and its sensibility 33 mm. per microvolt.

The Luminosity Curve Solution.—The luminosity curve solution was worked out by trial with the spectrophotometer, to conform quite closely to the luminosity curve as determined by Ives. At the same time the number and character of the constituents was such that by altering their relative proportions the transmission curve could be altered to correspond quite closely to the characteristics of the Nutting curve, or toward the characteristics of individual curves in the groups of which the ones quoted are average. This first approximation to the working solution was composed as follows:

Cupric chloride	60 grams.
Cobalt ammonium sulphate	7.5 grams.

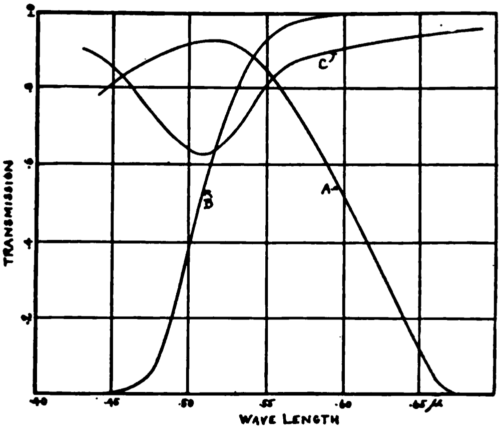

Fig. 3.

Spectral transmissions of constituents of luminosity curve solution. *A*. Cupric chloride. *B*. Potassium chromate. *C*. Cobalt ammonium sulphate.

Potassium chromate	1.7 grams.
Nitrid acid (1.05 gr.)	15 c.c.

The chromate should be dissolved separately and the acid added to it. These constituents have been carefully selected for permanence and other practical qualities.

In Fig. 3 are shown the transmission of the constituents separately. This solution has a transmission closely that of the Ives curve and it will be easily seen that it should be possible by altering the amount of the cobalt constituent to remove the chief difference between that and the other experimental luminosity curve obtained by Nutting and by changing the copper or potassium chromate to shift the curve bodily toward red or blue. The Nutting curve we find is very accurately copied by the following composition.

Cupric chloride	68 grams.
Cobalt ammonium sulphate	14 grams.
Potassium chromate	19 grams.
Nitric acid (1.05 gr.)	15 c.c.
Water to	1 liter.

The Arrangement of Apparatus and Method of Reading.—Fig. 4 shows the arrangement of apparatus to scale, as set up in our physical photometer room, a basement room 10 × 10 feet square, where the temperature is reasonably constant.

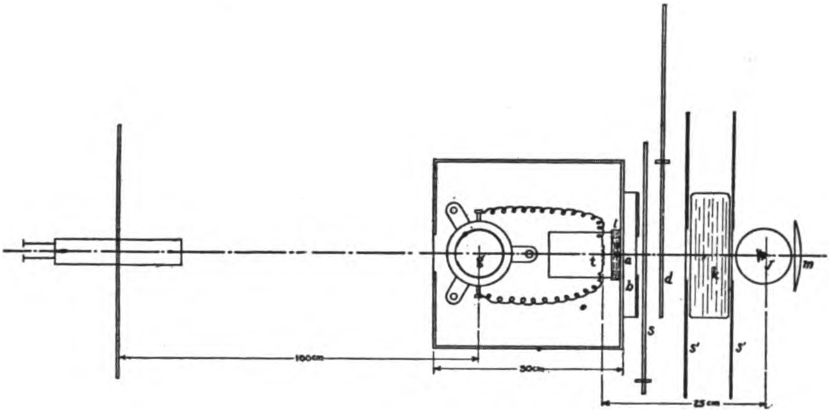

Fig. 4.

Diagram of thermopile artificial eye. *t*, thermopile; *l*, luminosity curve solution; *g*, galvanometer; *j*, lamp; *s'*, screens; *k*, protective water tank; *s*, shutter; *d*, sector disc; *b*, ledge holding absorbing media to be measured; *m*, mirror.

The thermopile *t*, the luminosity curve solution in a one centimeter thick glass tank *l*, and the galvanometer *g*, are all placed close together on the top of a concrete pier in an enclosing box. The box has a small aperture *a*, facing toward the 100-candle-power stereopticon lamp *j*, 25 cm. distant. The radiation from the latter passes through openings in two tin screens s^1 and through the water tank *k*. This latter was adopted originally for the purpose of keeping the surroundings of the thermopile from unnecessary heating, and is, we find, essential but for this purpose and to completely obstruct infra-red radiation. A shutter *s* and a sector disc *d* are interposed between the luminosity curve solution and the water tank. The absorbing solutions to be measured are placed on a ledge *b*. *m* is a concave mirror which may be placed behind the lamp to increase the size of the deflections when desired.

The apparatus as shown in the diagram is arranged for the measurement of absorptions. It can, however, be just as well utilized for measuring the intensities of light sources. With the point source carbon lamp, which gives approximately 45 candle power at "4-watt" color, we obtain deflections of 7 centimeters without the concave reflector, or as much as 20 with it. For the measurement of absorption the sensibility may be greatly increased by the use of a convex lens between light source and thermopile. Smaller light sources could be brought considerably nearer the thermopile. Actually we find no advantage in going over five centimeters with the deflections, so that we believe the sensibility of the apparatus in its present form is sufficient for all ordinary purposes. Candle-powers as low as 8 can be measured accurately.

The chief impediments to accuracy in physical photometry we have found to be mechanical disturbance, drift and lack of exact proportionality between stimulus and response in the galvanometer. Mechanical disturbances depend for their magnitude upon the location of the laboratory and the location of the galvanometer in the laboratory. With the d'Arsonval galvanometer magnetic disturbances are not to be feared under usual conditions; purely mechanical ones are slight in the ordinary basement and, where heavy machinery is near, we find the Julius suspension very effective. In short, the arrangement we have adopted is entirely practical from this standpoint for the average laboratory.

Drift of the galvanometer-thermopile system we find by far the most serious trouble we have to contend with. Even in a room at unusually constant temperature there is apt to be a slow creep of the zero, amounting sometimes to several per cent. of the reading during the time taken for a deflection and the return to zero. We believe that much of this might be eliminated by enclosing the galvanometer and thermopile in a thermostat, as could be done easily with the whole system occupying the small space it does here. Experiments along this line are now in progress in connection with another problem. Meanwhile we have found it easy to meet this difficulty by making the manner of reading such as to automatically eliminate the effect of drift. To do this we make our readings on a timed basis. We have found with our system that by allowing exactly the same time interval between the first zero reading, the deflection and the final zero reading, that the true zero may be taken as the mean of the first and last readings. We find 30 seconds a convenient and sufficient period of exposure. In addition to this procedure we so arrange that all our deflections are of approximately the same size, securing this condition by the use of the sector discs (operated by a distant motor to avoid magnetic disturbances).

Any lack of exact proportionality between stimulus and deflection such as is caused by an off-center suspension of the galvanometer coil, is also neutralized by the use of the sector disc to maintain the deflections of the same size. Another source of error, which falls under the same head, is a slow change in the sensibility of the system, which we notice at times. The exact cause of this we have not determined. It may lie in the gradual heating up of the entire thermopile, or it may lie entirely in the galvanometer. We find that this effect may usually be reduced by exposing the thermopile steadily for some minutes before beginning regular work. It is, however, our practice, in addition, to alternate the readings on the standard and test lights so that any effect on the result is eliminated. We have good reason to believe that most of these difficulties are to be ascribed to the very severe conditions with respect to acid atmosphere and dust peculiar to our laboratory, situated in the midst of gas works.

By following these precautions we have no difficulty in securing a precision of better than one per cent.

We may remark here parenthetically that the attainment of this degree of precision with a degree of sensibility adequate to measure the usual light sources suggests the desirability of applying this physical method to precision photometry even where there is no problem of color difference. For instance the intercomparison of standard lamps. Under good laboratory conditions a precision three or four times as good as we attain should be easily possible.

Since the greater part of the work here reported was completed we have made a trial of a vacuum thermocouple with very promising results. This, constructed by Dr. E. Karrer and in general agreement with the design of Dr. A. H. Pfund,[8] consists of a single junction (with a second similar junction for compensation) of BiSn, BiSb alloys, in a glass container exhausted with the aid of a charcoal evacuator. This junction has a very small mass, but is connected to a rather large mass of metal intended to act as a heat reservoir.

We find this junction to be more definite in action and freer from drift and changing sensibility than the exposed type. Where it is possible to make or obtain thermocouples of this type we believe they will give great satisfaction.

We mention the trial of this extra junction in order to suggest that a more systematic study of the galvanometer-thermopile system than we have made may be expected to greatly improve on the precision obtained by us.

The Changes Found Necessary in the Original Luminosity Curve Solution.—With the luminosity curve solution matching the Ives curve as described, the first set of color differences measured were those given by the yellow Fabry solution. It was found that over the range represented by the commoner illuminants and standards, namely, from the Hefner to the "1 watt per candle" tungsten, the agreement between visually determined and physically determined values was practically perfect.

Beyond this range of color difference, however, a progressive divergence appeared, greater where the blue end of the luminosity curve was in question than where the red end was most used. Thus on the "comparison lamp" side[9] the difference between visual and physical values approached one per cent., at the end of the observed curve, on the "test lamp" side, where the color difference amounted to that between a "4-watt" and a "half-watt" lamp, the difference was as much as two per cent. Now, although these differences fall well within the scattering points obtained by a group of selected observers, we considered it undesirable to stop short of exact agreement and, therefore, undertook a cut and try modification of the luminosity curve solution.

As the first step in this we measured the two "test" colors. These we found to measure two per cent. off the visual value, the yellow solution measuring too small. We had then at our disposal several means of effecting a correction. We could decrease the concentration of the cupric chloride, thereby making the system more red sensitive. Or we could increase the concentration of either the cobalt or the chromate. Bearing in mind that the chief difference between the Nutting and Ives curves lies in the blue-green, the correction decided upon was an increase in the concentration of the cobalt. Such an increase was found by trial as would make the two test colors read alike.

This new solution was then tried out on the Fabry yellow, with the result that the discrepancy at the test lamp end was found little affected. It was soon evident why this was the case. The spectral transmission of the green test color is such that a change in the concentration of the cobalt constituent is very effective on it. The color difference introduced by the tungsten lamp is however relatively much less sensitive to this change than it would be to a change farther from the center of the spectrum. This gave the clue to the next change, namely, an increase in the concentration of the potassium chromate. After several trials a balance was hit which behaved equally well with all the test color differences. The final solution has the composition:

Cupric chloride	60.0 grams.
Cobalt ammonium sulphate	14.5 grams.
Potassium chromate	1.9 grams.
Nitric acid (1.05 gr.)	18.0 c.c.
Water to	1 liter.

[An essential part of the absorbing means is the protective water layer of at least 2 cm. thickness.]

The spectral transmission is shown in Fig. 1 (full line), plotted to a maximum value of unity. This curve differs from the experimentally determined ones in being shifted somewhat toward the red end of the spectrum, a point which will be discussed presently. The transmission of this solution is represented very accurately by the following equation:[9]

$$L_\lambda = A\left(\frac{R_1}{\lambda}e^{1-(R_1/\lambda)}\right)^\alpha + B\left(\frac{R_2}{\lambda}e^{1-(R_2/\lambda)}\right)^\beta + C\left(\frac{R_3}{\lambda}e^{1-(R_3/\lambda)}\right)^\gamma$$

where

$$A = .999,\quad R_1 = .556,\quad \alpha = 200,$$
$$B = .04,\quad R_2 = .465,\quad \beta = 400,$$
$$C = .095,\quad R_3 = .610,\quad \gamma = 1{,}000.$$

Performance.—The final physical photometer measures the two test colors equal to within one half per cent. On the Fabry solutions the agreement between visual and physical values is everywhere well within one per cent. and the calculated value drawn through the visual points lies nowhere more than one half per cent. away from the physical values. This agreement we feel justified in calling complete, and, as stated above, we believe that since these test color differences are measured correctly, all other ordinary color differences of the kind met with in practical photometry (which excludes monochromatic lights) will also be measured satisfactorily. The visual, calculated and physical values for the Fabry solutions are shown in Figs. 5 and 6. These data indicate of course the accuracy to be expected in the measurement of the various light sources which the solutions counterfeit in color.

DISCUSSION.

It is not out of place to mention that the physical photometer is extremely simple and convenient in operation. It has been so arranged

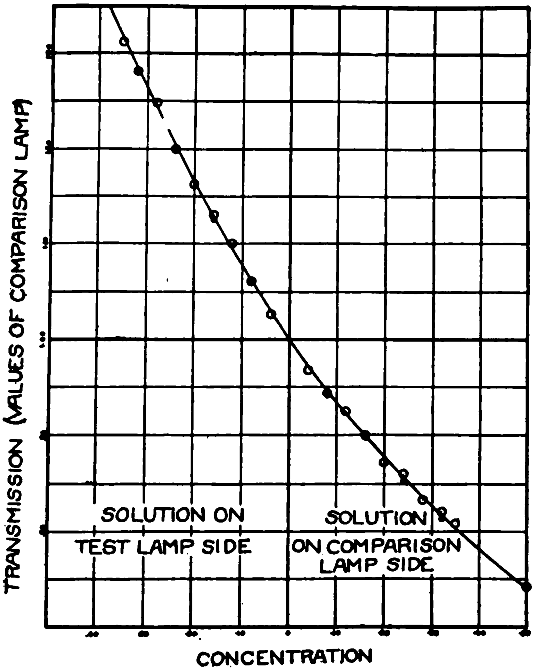

Fig. 5.

Visual and physical photometer values of Fabry yellow solution compared. Circles, visual points; full line, calculated curve; dots, physical photometer points. The color range represented is from the Hefner, at the right, to the "half watt" tungsten, at the left.

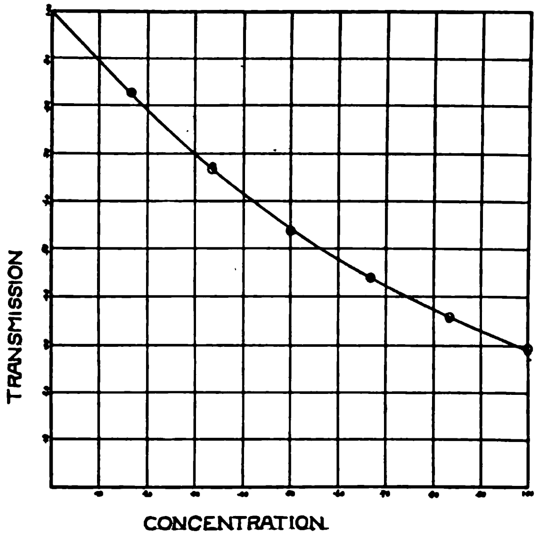

Fig. 6.

Visual and physical photometer values of Fabry blue solution compared. Circles, visual points; full line, calculated curve; dots, physical photometer points. The color range represented is from the standard carbon lamp, at the left, to the "half watt" tungsten, at the right.

that a single person can operate it perfectly. What has heretofore been a task for a group of five or more men, with a complete photometric track and accessories, can now be done by one man in a tenth the time.

The point perhaps of chief importance for discussion is the character of the luminosity curve demanded to secure the agreement between the visual and physical values. Why is it shifted toward the red end of the spectrum as compared with the directly determined ones? The explanation may lie, as already suggested, in the inherent difficulties of the direct determination. Or again it may be that our large group of observers on whom the visual values depend have a somewhat different average from the much smaller groups used in the luminosity curve determinations.

Another question of particular interest to the writers is why in our recent determination of the mechanical equivalent of light[10] the evidence was in favor of a curve shifted more toward the blue than that now indicated. The decision in favor of the bluer curve was made on the basis of the apparent better agreement, when such a curve was used, between the two methods of attack, in one of which (B) we measured the radiation transmitted by the luminosity curve solution, in the other (C) the intensity of a monochromatic green radiation.

With a view to tracing out the cause of the discrepancy which would exist were the luminosity curve as here determined employed in that investigation, we have measured on the physical photometer the transmission of the monochromatic green solution there used. We have performed the measurement both with the Nutting curve and with the new one. With the Nutting curve solution the transmission measured .0463, with the new curve .0441, the visual determined value being .0437. Now bearing in mind that the physical photometer cannot in its present form be expected to measure monochromatic light exactly right, this agreement of better than one per cent. using the new luminosity curve, shows conclusively that our visual and physical photometric work is throughout very satisfactorily consistent.

But more than that it shows that the discrepancy between the mechanical equivalent values must of necessity lie in the experimental apparatus and manipulation. No question of photometric method or of physiological or other obscure factors is at issue. Since the luminosity curve solution gives the ratio of the green light to the "white" exactly as used the new physical photometer might have been employed in the mechanical equivalent study instead of the eye and the two methods would become identical and of necessity would agree.

The answer to this riddle has fortunately been found through the accidental omission of the protective water tank in some measurements undertaken with the physical photometer. These indicated at once what has since been verified, that there must be an infra-red transmission band in the luminosity curve solution as used in the mechanical equivalent investigation. The effect of this is to give too large a value to the energy measured by that method called (*B*).

Fortunately, as was emphasized in the account of that study, the data were obtained in such a way that they are available for any re-calculation that a change in the units or luminosity curve might later render necessary. It has therefore been possible to correct the mechanical equivalent value as the result of making one comparatively simple measurement. That measurement is of the radiant luminous efficiency of the "4-watt" carbon lamp. As previously made with the unprotected "Ives" solution (with which the actual measurements were made, and then corrected to Nutting curve values) its value was .0049. As now determined with the protective tank of water and the new luminosity curve solution, its value is .0043. This means that the value for the lumens per watt of the most efficient light, as determined with the "Ives" solution is to be increased by 12 per cent. The corrected (Ives curve) figure by method (*B*) thus becomes 563.7 × 1.12 = 631.

The use of the new luminosity curve also affects the value by method (*C*), since the luminous efficiency of the green mercury radiation is now reduced to 97.5. Applying this to the quantity tabulated as "*m*" in the mechanical equivalent work, we obtain the figure 630. In short, the effect of the information derived from the development of the physical photometer is to rather firmly substantiate a luminosity curve shifted somewhat toward the red as compared with the experimentally obtained ones, and to harmonize all our previous data on the mechanical equivalent of light. *As an additional result of our work we therefore announce as the corrected value of the mechanical equivalent of light*

1 lumen = .00159 watt of luminous flux.

(The new value is 2 per cent. lower than the old.)

Satisfactory as is therefore the final result of the investigation of physical photometry, it must not be overlooked that the actual luminosity curve which is worked to is only determined by the transmission of a certain inorganic salt solution. We would therefore conclude this discussion by emphasizing the importance, both from the standpoint of developing the physical photometer and for the more accurate fixing of the mechanical equivalent of light, of securing a more accurately determined luminosity curve directly, using a very large number of observers.

This is a task which could be undertaken with especial fitness by such an organization as the Bureau of Standards. Until the luminosity curve of the spectrum is completely determined and exactly matched in the sensibility curve of a radiometer the physical photometer can be used with entire safety only for those classes of color difference for which it has been proved to agree with the visual scale. It is in fact to a certain extent empirical in its present form. Where there is any question it will be advisable to work over rather small ranges of color difference from standards calibrated by the visual method. Obviously monochromatic radiations can hardly be expected to measure correctly with any except an exact copy of the luminosity curve.

We emphasize these limitations of the physical photometer here described in order to show in which direction lies the research work which shall keep the physical photometer abreast of the probably more exacting needs of the future. As far as the present is concerned the emphasis is to be placed on the fact that we have here in practical use a physical average eye, proven capable of measuring the more usual color differences met with in practical photometry, with the same results as are given by the method of visual colored light photometry used by us.

Summary.

1. A practical physical photometer has been developed suitable for colored light photometry in the standardizing laboratory.
2. A spectral luminosity curve has been determined slightly different from one previously published.
3. A corrected value is obtained for the mechanical equivalent of light.

Physical Laboratory,
The United Gas Improvement Company, Philadelphia,
April 20, 1915.

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[1] See Ives, Physical Photometry, Trans. Illuminating Engineering Society, No. 1, 1915, p. 101.

[2] Fery, Journal de Physique, August, 1908.

[3] Ives, Photometry of Lights of Different Color, Phil. Mag., July, September, November, December, 1912.

[4] Nutting, Visibility of Radiation, Trans. I. E. S., No. 7, 1914, p. 633.

[5] Ives and Kingsbury, On the Choice of a Group of Observers for Heterochromatic Measurements, Trans. I. E. S., 1915.

[6] Ives and Kingsbury, Experiments on Colored Absorbing Solutions for use in Heterochromatic Photometry, Trans. I. E. S., No. 1914.

Ives and Kingsbury, Additional Experiments on Colored Absorbing Solutions for use in Heterochromatic Photometry, Trans. I. E. S., 1915.

[7] Fabry, A Practical Solution of the Problem of Heterochromatic Photometry, Trans. I. E. S., June, 1913, p. 302.

[8] Pfund, Phys. Rev., XXXIV., No. 3, p. 228.

[9] The derivation of this equation will be treated in a separate paper.

[10] Ives, Coblentz and Kingsbury, The Mechanical Equivalent of Light, Phys. Rev., April, 1915, p. 269.

A PRECISION ARTIFICIAL EYE.

By Herbert E. Ives.

The most attractive solution of all problems of measurement which depend upon the characteristics of a normal or average eye is to embody these characteristics in some entirely physical instrument. Among these problems may be mentioned as most important the measurement of luminosities of lights of different color, and the measurement of color. In each of these cases the value obtained by a single observer, by whatever method employed, is apt to be of little value. Numerous observers must be called upon in order to secure an average value. If, however, the properties of the average eye can be reproduced in an artificial physical eye this troublesome and often impracticable procedure may be avoided.

In a recent paper[1] a thermopile artificial eye was described, consisting of a sensitive thermopile over which is placed an absorbing solution whose transmission copies quite closely the spectral luminosity curve of the average eye. One objection which might be raised to this instrument where absolute precision is in question, is that the "luminosity curve solution" must necessarily be merely an approximation to the experimentally determined luminosity curves, and therefore not applicable to all kinds of colors. Furthermore, if it is desired to copy more than one curve, as would be the case if color measurement on the three-color basis were attempted, the labor of working out the numerous absorbing solutions may be expected to be well nigh prohibitive.

The present paper describes a thermopile artificial eye that is not open to these objections. It is a precision instrument in the sense that any wave-length sensibility curve may be exactly copied. Once the instrument is constructed the labor of copying additional curves of any type is comparatively trivial.

The apparatus is a modification of the "Apparatus for the Spectroscopic Synthesis of Color," described some time ago.[2] It consists essentially of a spectrometer forming a spectrum which is passed through a template and then recombined upon a sensitive thermojunction. By means of templates of various shapes the radiation may be evaluated in any desired way, as luminous flux, as red, green, or blue sensation, etc. The possibility of doing this was discussed by Strache,[3] in his proposal to establish the standard of light radiometrically, but to the best of my knowledge has never been tried experimentally, probably owing to the lack of sufficiently sensitive means for the measurement of the small amounts of radiant power involved.

Fig. 1 exhibits diagrammatically the complete apparatus. The image of a filament or extended light source *L* is formed on the slit *S* by means of a lens. A spectrum of this is formed by the prism *P* at S^1. Over this spectrum is a template, which may be in the form of a rotating disc, or which may be a flat stationary plate, as will be discussed presently. Close to the template is a lens or lens system, whose function is to recombine the spectrum, forming an image of the prism face in the color of the recombined light upon the thermojunction *J*. Further details of the apparatus will be described in the discussion of their functions. Detailed information on the method of calculating the openings of the templates, etc., is to be found in the paper previously referred to.[2]

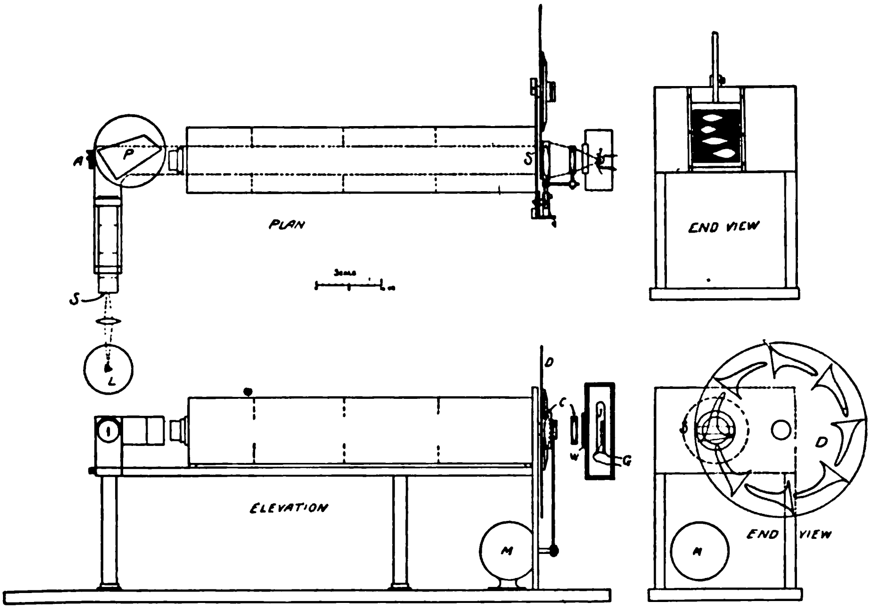

Fig. 1.

Diagram of the precision artificial eye. *L*, light source; *S*, slit; *P*, prism; *S′*, spectrum; *D*, disc template; *C*, condensing lenses; *W*, tank for absorbing solution; *J*, thermopile; *G*, galvanometer lead; *M*, (clock or hand) motor; *A*, adjusting screw for prism table.

By far the most important point to be determined in connection with the development of such an instrument is whether adequate sensibility can be obtained. The degree of sensibility required is very high. The radiation to be measured lies of course entirely in the visible portions of the spectrum, a region of very low emission in all the artificial light sources which would be the subject of measurement. Moreover the intrinsic brilliancy, which is a definite limit to the amount of energy which may be received through a dispersing apparatus, is with many light sources quite low. These points are illustrated by noting that radiometric studies of the visible spectrum have been few, chiefly confined to light sources of high intrinsic brilliancy like the Nernst glower or incandescent electric lamps. These have intrinsic brilliancies of the order of magnitude of 100 or more candle power per square centimeter, while the glass mercury arc or the Welsbach mantle (in the study of which this instrument is to find its immediate use) drop below 5 of the same units.[4]

A detailed study of the factors conditioning sensibility brings out several points of interest. For a light source of given intrinsic brilliancy it is obvious that the amount of energy focused on the thermojunction is directly proportional to the width of slit employed (it being understood that the entire slit width is filled with the image of the light source). It is also directly proportional to the angular extent of the telescope lens as viewed from the point of formation of the spectrum. It is directly proportional to the vertical height of the spectrum utilizable. It is of course dependent also upon the number of reflecting and absorbing media used in the prism and lens system.

Assuming that the spectrometer system has been so designed that a spectrum is formed (of sufficient length to be practically handled by a mechanically cut template), using the maximum width of slit permitted by the purity necessary, of maximum feasible telescope aperture, as conditioned by the necessary degree of definition; utilizing the greatest vertical length of spectrum, as conditioned by the curvature of the slit image and the length of the slit image which is of uniform brightness; and possessing the minimum number of light obstructing surfaces,—the rest of the problem is that of attainable radiometric sensibility.

Probably the most sensitive means for measuring radiation, suitable for the present problem, is furnished by the thermopile with appropriate galvanometer. Using this combination the problem of sensibility consists of two parts, the thermopile problem and the galvanometer problem.

The thermopile problem is of particular interest, for this reason; that with the optical arrangement assumed the attainable sensibility is limited practically to the intrinsic sensibility of a single junction. This is made clear by considering first the recombined spectrum as entirely received upon a single junction. Suppose now it is desired to use *n* junctions; the image of the prism face would have to be *n* times larger, each junction would receive 1/*n* times as much radiation; in other words the thermoelectromotive force developed would be the same. If the resistance of the *n* junctions is the same as that of one junction the current developed will be the same in the two cases. The only possible gain in the use of many junctions therefore lies apparently in the decreased resistance which might be obtained by joining the junctions in parallel. The resistance of a single junction is however so low in comparison with that of the galvanometer that no great gain in sensibility may be expected by the use of multiple junction piles.

This limited condition naturally directs attention to means for securing the maximum intrinsic sensitiveness of a thermojunction. In the present case use is made of a BiSn-BiSb thermojunction of the evacuated type, constructed by Dr. E. Karrer in general conformity with the design published by Dr. A. H. Pfund.[5] This junction, of alloys having a higher thermoelectric power than any pure metals commonly used, is increased in sensibility five to six times by the process of exhausting the containing vessel. It is equivalent to ten or twelve bismuth-silver junctions. The actual junction used has for receiver a tin plate approximately two millimeters square. The image of the prism face, formed by a system of three achromatic lenses, is of closely the same area, but being round projects a little beyond the junction at each side. Obvious improvements would be to furnish the junction with a round receiving plate, to secure the equivalent lens system with fewer glass surfaces, and if possible reduce the size of the prism image, since the sensibility of a junction only increases with the square root of the area. With all these changes made however it is doubtful whether the sensibility could be more than doubled; hence the use of the vacuum junction gives at least five times the sensibility to be expected from any other form now available. This factor, in the apparatus constructed, just makes the difference between adequate and inadequate sensibility.

The galvanometer employed is an iron-clad Thomson instrument designed by Coblentz. Its resistance is 5.1 ohms. Its sensibility as ordinarily used by us is from 2 to 5×10^{-10}. amperes per mm. deflection, with a period of three to six seconds. The galvanometer is enclosed in a series of soft iron pipe shields, to protect from magnetic disturbances (with which we are not however much troubled in our laboratory), and is carried on a Julius suspension to protect it from mechanical vibration. This latter is a very serious problem with us, as a 20-inch gas main direct from the near-by gas pumping station makes a right angle turn only thirty feet from the laboratory. Every throb of the pump was reflected in a centimeter jerk of the galvanometer when this was mounted merely upon a heavy pier. The Julius suspension, constructed closely in accordance with the original publication of Julius,[6] entirely eliminated this trouble. The control magnets are mounted partly on the suspension (which is locked to a surrounding ring when these are being adjusted) and partly on the top of the shielding system. The latter magnets are used almost solely for turning the mirror to bring it in the proper part of the scale. The whole system—galvanometer, shields, etc.,—is mounted inside an enclosing box which prevents air drafts from starting long period swinging. These details are mentioned in order to show that the apparatus, although possessing high sensibility, is not impractical in form for the average laboratory, where conditions should be much better than in our own.

The first template tried was in the rotating disc form, shown in the figure at *D*. This was cut to the visual luminosity curve as recently fixed upon by work reported in this journal,[1] correcting for the absorption of the prism, shown in Fig. 2. Using a carbon lamp as the light source, and a slit width of about 50 A.U. in the green, deflections of five or six centimeters were obtained, demonstrating the feasibility of the scheme.

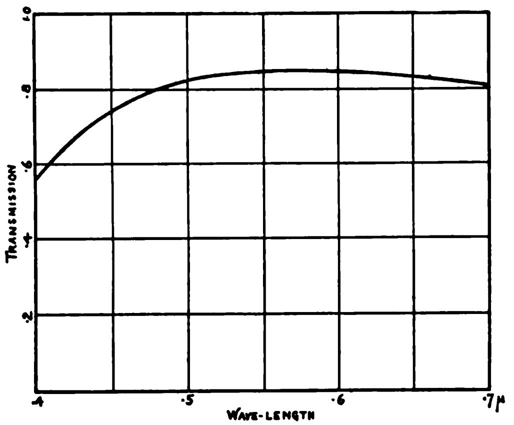

Fig. 2.

Spectral transmission of prism used in precision artificial eye. (Measurements made on block of identical glass supplied by makers of prism. Thickness 9 cm.—that of light path through prism—refractive index 1.6181.)

It had been anticipated, however, that one of the practical difficulties would be the presence of scattered radiation, due to the hundred-fold greater amount of invisible than visible radiation. It was thought to eliminate this in part by the use of a water tank *W* before the thermojunction, but it was soon suspected that some still remained. A test experiment verified this suspicion. A solution of iodine in carbon disulfid was prepared of such concentration that only the deep red and violet were transmitted. The red and violet ends of the spectrum formed at S^1 were covered with opaque screens, and the light exposed. A deflection of about ten per cent. that previously found was now obtained. This amount of scattered radiation in spite of the presence of the water tank, and the great length of the spectrometer system, appears to the writer to cast considerable doubt on the accuracy of data on the visible end of spectral energy distribution curves obtained without the use of most elaborate means for eliminating such errors.[7]

To remove the disturbing infra-red radiation recourse was made to a screen of copper chloride, in place of the water at W. A three per cent. solution of one centimeter thickness was found best suited to meet all requirements. When using this screen of course the template transmissions must all be increased by the reciprocal of the transmission of the copper chloride. This involves the exact determination of this transmission by the spectrophotometer, whereby an undesirable but apparently unavoidable element of uncertainty is introduced. The necessity for uniform temperature also enters owing to the temperature coefficient of transmission of the copper chloride. It is possible that a copper glass would serve in place of the solution and be free from the last objection, which however is not at present serious.

As the labor of cutting the disc template is considerable it was decided to make the new curve in a fixed form. This is possible in the present arrangement where it was not in the original synthetic color apparatus[2] because in the latter the eye was used at the observing slit, and the aperture of the eye imposed an impractical limitation to the possible slit length. Where it is possible to cast upon the slit S a long uniform image, such as that from an incandescent lamp filament, the use of a fixed template is much the simplest scheme. It is only necessary to be sure that the whole width of the spectrum used receives light from the whole of the prism face, which may be tested by moving the eye up and down the vertical length of the spectrum. An advantage of the fixed template is that no motor is necessary. The latter, by the way, must in working near a sensitive galvanometer, be clock or hand driven.

To cut the new templates a photographic method was employed. The curves desired were calculated and then laid out on a large scale with drawing instruments. The parts desired opaque were painted black, and the reference wave-length line (.5461) clearly marked at the ends of the sheet. This was photographed down to the correct size and the negative, which was made thin, was painted in the exposed parts with opaque pigment. From this a thin print on glass was made which was in turn painted with opaque paint by carefully following the edges of the exposed portions. By taking such precautions as printing in a printing frame with a black velvet back, and not carrying the development far it is possible in this way to secure beautifully clear and (with ordinary draftman's skill in the painting) accurate templates. Fig. 3 shows the template so constructed. It has upon it the luminosity curve of the spectrum, and the red, green and blue Koenig sensation curves. The peculiar spreading at the red end is called for to offset the absorption of the copper chloride.

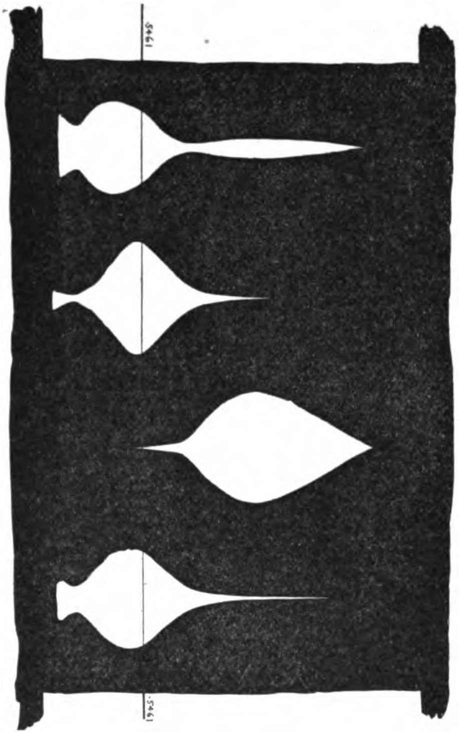

Fig. 3.

Drawing for stationary template. Top, luminosity curve. In order, blue, green and red sensation curves.

This glass template was mounted with adjustable clamps upon a brass frame sliding in accurate tracks, as shown in the figure (the upper "end view"). Tests of this arrangement showed entire absence of scattered radiation. It was then tried out on the same test colors used in the work on the thermopile artificial eye previously described.[1] With the standard carbon lamp it was found possible to obtain deflections of 20 centimeters and over (workable deflections were obtained with a Cooper-Hewitt mercury arc), but more satisfactory results were given by keeping the deflections down to three or four centimeters by the introduction of extra resistance in the galvanometer circuit. Measurements made on the test colors showed very satisfactory agreement with the visual values.

In addition to the measurement of relative luminosities this instrument may be used for color measurement by the three-color system. It is only necessary to have three templates each cut to represent the mixing proportions throughout the spectrum of one of the chosen primaries and measure the relative deflections through these. The logical primaries to choose are the fundamental sensations, for instance as determined by Koenig.[8] (Measurements in terms of these may be transformed into the values obtained by using other primaries or into hue, luminosity and purity values.) These curves have been reproduced in the glass template shown in the figure, the energy distribution of a black body at 5,000° abs. being taken as "white," and have been tried out for actual color measurement.

A 3.1 w.p.c. carbon lamp was measured, the values for the three sensations coming out:

$$R = 50,$$
$$G = 43,$$
$$V = 7.$$

Values which I calculated some years ago,[9] on an assumed distribution of energy for the carbon lamp were:

$$R = 51,$$
$$G = 41,$$
$$V = 8.$$

It will be seen that these values are reasonably close to each other. There is at present no criterion by which to decide that the measured values are not the correct ones. This measurement of color is intended to be merely illustrative. A table of values on artificial illuminants may later be compiled and published.

Certain refinements are suggested on this first apparatus. For instance, the possibility of scattered light affecting the results could be met by covering each template opeining with a colored glass approximating the curve desired, letting the shape of the opening merely take up the difference between the glass transmission and the true curve. Thus a thin sheet of gold ruby for the red, a sheet of "pot" green glass for the green, a piece of "signal blue," for the blue would admirably meet the requirements. In each case of course the spectral transmissions of the glasses would have to be accurately determined.

Now as to the uses of this precision artificial eye. First its uses in photometry. Here its chief application will be in the measurement of the transmissions of colored absorbing media to be used in eliminating color differences upon the photometer. With templates cut, as has been explained, exactly to a legalized luminosity curve of the spectrum, an instrument of this type is calculated to become a standard artificial eye, suitable for the foremost standardizing laboratories.

Second, its uses in color measurement. Here its chief application will lie in the measurement of the colors of illuminants. The general loose descriptions of lights as "snow white," etc., can be superseded by exact evaluation in definitely established units, which may be made without dependence upon the visual characteristics of a chance observer, or the necessity for comparison with a concrete color standard. The colors of glasses or other transmitting media may be determined with this instrument. These may be measured over some convenient light source, such as a carbon lamp, or if desired the templates may be so cut that while actually using a source of known energy distribution quite different from white light the results are in terms of the white light transmissions. In order to do this it is only necessary to determine with accuracy the spectral energy distribution of some convenient light sources in the visible region, a task of some delicacy but nearer practicability now than formerly.

As an illustration of a technical application of the device may be suggested the inspection of colored glass such as "daylight glass." Having determined what a correct sample (as fixed by the use of this same instrument as a synthetic color producer)[2] should measure when interposed over any convenient reproducible standard light source this value could be plotted on a color triangle, and to establish a tolerance limit a circle of size to be agreed upon by the parties interested could be drawn from this point as center. The sum of the three measured values would afford a check on any admixture of black which might decrease transmission without altering the color. Or a measurement of total transmission could also be made with the luminosity template. By this means the measurement or inspection of colored glasses could be made an exact problem. (A similar scheme giving results in entirely arbitrary units could be worked out, using three color-screens of overlapping transmissions. The instrumental sensibility required for this scheme would be far less than for the precision device.)

The description of the instrument as constructed is given here chiefly to show that such a device is actually feasible, with the instrumental means now at the disposal of the physicist. It is limited in its application to those cases where a relatively large amount of light is available, as has been indicated, but these cases are sufficiently numerous to offer a large field of usefulness. It is to be confidently hoped that the near future will disclose means for considerably increasing the sensibility, perhaps by as much as five or ten times. It is to be expected that a detailed study of the present instrument will show possibilities for considerable improvement even with present radiometers. Such improvement as increased aperture and reduction of the number of reflecting surfaces would help materially. The thermopile can undoubtedly be somewhat better calculated for its purpose, by making the receiver round, and perhaps under some conditions by a parallel connection of several junctions. There is besides the possibility that some more sensitive thermojunction will be developed (for instance bismuth-tellurium) which would be entirely satisfactory as a vacuum instrument for use with visible radiation only, restrictions which while serious in some work would not be at all so for this purpose. Could the wave-length sensibility curves of sensitized photo-electric cells[10] be controlled another form of radiometer might be utilized. Whatever may be the development of the future the writer wishes to emphasize that the first step has been taken, a precision artificial eye has been constructed and is in use.

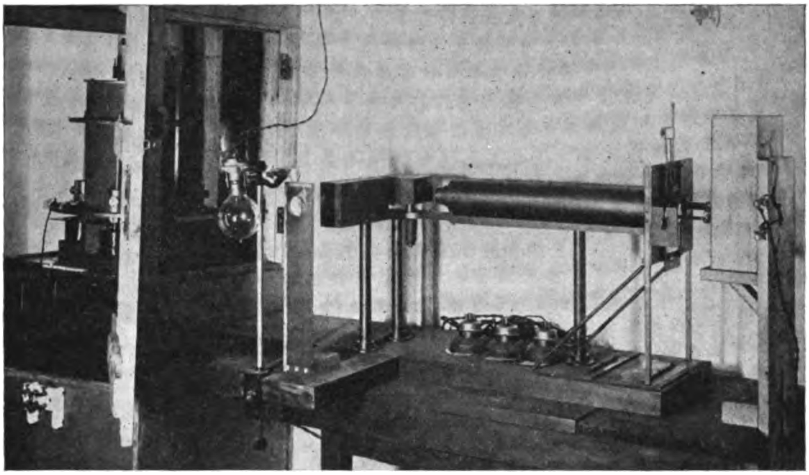

Fig. 4.

Photograph of precision artificial eye.

I take pleasure in acknowledging my indebtedness to Mr. E. J. Brady, Mr. E. F. Kingsbury and Dr. E. Karrer, who have cooperated with me at one stage or another in the development of the instrument. Special acknowledgement is also due to Mr. Charles B. Smith, whose mechanical skill and practical suggestions contributed substantially to the success of the work.

PHYSICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY,
PHILADELPHIA, PA.
May 7, 1915.

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[1] "Physical Photometry with a Thermopile Artificial Eye," Ives and Kingsbury, PHYS. REV., 1915.

[2] "An Apparatus for the Spectroscopic Synthesis of Color," Ives and Brady, Journal of the Franklin Institute, July, 1914, p. 89.

[3] Strache, Proc. American Gas Institute, 2, 401, 1911.

[4] "Measurements of Intrinsic Brightness by a New Method," Ives and Luckiesh, Electrical World, Feb. 16, 1911, p. 438.

[5] "A Sensitive Black-Body Vacuum Thermojunction," A. H. Pfund, PHYS. REV., XXXIV., p. 228, 1912.

[6] Julius, Annalen der Physik, 56, p. 151, 1895.

[7] R. A. Houstoun (Proc. Roy. Soc. Edin., Vol. XXXI., 4, No. 36, 1911), in agreement with this observation, found it necessary to adopt elaborate precautions to eliminate stray radiation when working in the regions of low emission.

[8] "Die Grundempfindungen," etc., A. Koenig and C. Dieterici, Zeits. für Psychologie u. Physiologie, 4, p. 241, 1892.

[9] "Color Measurements of Illuminants," Ives, Trans. Illuminating Engineering Society, April, 1910, p. 189.

[10] "Wave-length Sensibility Curves of Potassium Photoelectric Cells," Ives, Astrophysical Journal, Vol. XL., No. 2, Sept., 1914, p. 182.

THE MOBILITY OF THE POSITIVE AND NEGATIVE ION AT DIFFERENT TEMPERATURES AND AT CONSTANT GAS DENSITY.

By Henry A. Erikson.

THE object in pursuing the present investigation was to obtain evidence as to what change takes place in the size of the positive and negative ion in air when the temperature is altered, the density of the air being kept constant.

Evidence that a change takes place at temperatures less than 0° C. is offered by the results obtained by Phillips[1] and Kovarik[2] who independently determined the mobility at different temperatures. These results, however, were obtained at constant gas pressure and, therefore, do not necessarily indicate what happens when the density is kept constant, since the conditions to which the ions are subject in the two cases are not the same.

The method used was Rutherford's alternating field method as modified by Franck and Pohl. This method, from the standpoint of convenience, is well adapted for an investigation of this kind.

Fig. 1 is a diagram of the apparatus and experimental arrangement. *A* is a cylindrical vessel that has a radius of 6.2 cm. and a depth of 3.2 cm. *B* is a circular plate that has a radius of 5 cm. This plate is supported by the insulated stem *C*, and through it is connected to a quadrant electrometer. In order to reduce heat conduction a portion of the stem *C* is of glass. One centimeter above *B* is another plate *D*, of same diameter as *B*. The opening in *D* has a radius of 3.8 cm. and is covered by a brass wire gauze having nine meshes to the centimeter. The ring *D* is supported by means of three rods of quartz. A small polonium plate is attached face up at the center of the gauze. Another plate *E* is placed 4 mm. above *D*, and is supported and insulated from *D* by means of the three quartz rods.

The rays from the polonium ionizes the air between the plates *D* and *E*, which are kept at a difference of potential of about 0.8 volt by means of the battery *F*. The positive or negative ions as the case may be are driven towards the gauze through which some of them pass and thus become subject to the alternating field that is produced when the tuning fork alternately connects *D* to the positive and negative poles of the battery *G*. The wires connected to plates *D* and *E* pass through two quartz tubes placed one inside the other. For determining the temperature, a constantine wire is connected to the copper wire attached to *E*. These two wires pass without touching through the outer quartz tube.

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[1] Phillips, Proc. Roy. Soc. LXXVIII., 1906, p. 167.

[2] Kovarik, Phys. Rev., XXX., April, 1910.

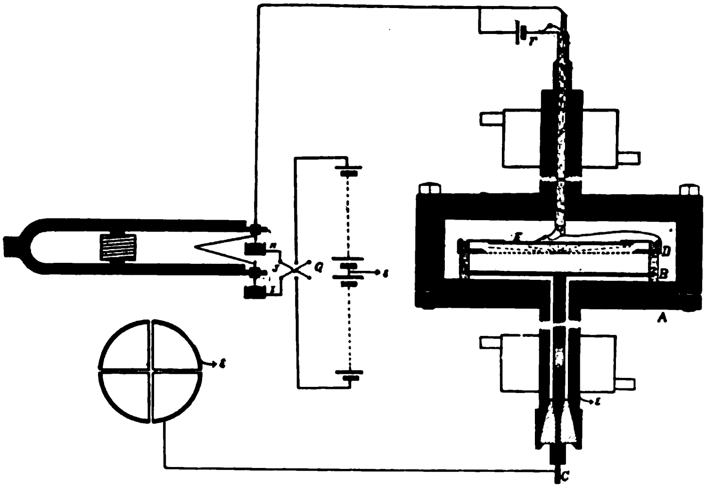

Fig. 1.

These tubes are held in place and made air tight by means of a hard wax. The ends of the upper and lower stems of the apparatus are kept at a safe temperature by means of water jackets placed as shown in figure.

This tuning fork method for shifting the polarity was found to be very satisfactory. *H* and *I* are two iron mercury cups of 8 mm. diameter. Contacts with the mercury in these cups are made through steel needles attached to the prongs of the fork. It is possible to adjust so that the mercury makes no perceptible vibration thus giving regularity of contact. Since it is difficult to secure the same interval of contact for each of the points a reversing key *J* was introduced and the average of an equal number of readings for each point was obtained.

By suitably adjusting the frequency of the fork and the potential of *G* some of the ions will reach the plate *B* before the field is reversed. The total charge then given to *B* in a given time may be measured by means of the electrometer.

This arrangement gives rise to the following relation:

$$q = it = i\left(\frac{t'}{2} - \frac{d^2nt'}{kv}\right), \qquad (1)$$

where

i = the current that flows through the gauze,

t = the time to charge the plate B to a given potential when the field between B and D is constant,

t' = the time to charge the plate B to the same potential when the field is alternating,

d = the distance between the plates,

n = the frequency of the fork,

v = the difference of potential between B and D,

k = the mobility.

In this equation d^2n/kv is the time consumed per second by the ions in passing from the gauze to the plate B.

From the above relation we see that:

$$\frac{2t}{t'} = 1 - \frac{2d^2n}{kv},$$

or

$$\frac{d}{dn}\left(\frac{2t}{t'}\right) = \frac{2d^2}{kv}, \text{ a constant.}$$

This shows that the current in the case of the alternating field which is proportional to $1/t'$ is a linear function of n the frequency of alternation. That this holds is borne out by experiment the results of which are shown graphically in Fig. 2. By prolonging the line until it cuts the y axis we obtain the value of n, the frequency, for which t' becomes infinite. In terms of this frequency

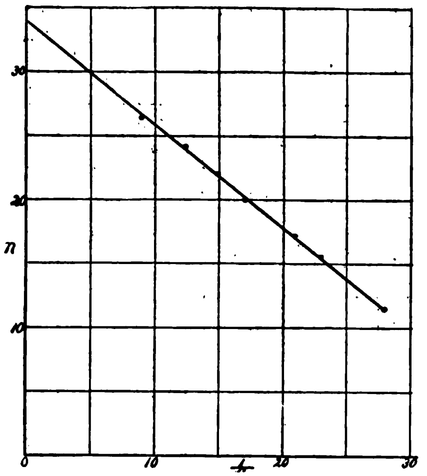

Fig. 2.

$$k = \frac{2d^2n}{V}.$$

The above method necessitates the changing of the frequency of the fork. As this, in the case of the fork used, was not convenient, the mobility was calculated by means of the equation

$$k = \frac{2nd^2t'}{V(t' - 2t)},$$

which is obtained by solving for k in equation (1). Since d, n and v are kept the same they may be determined once for all, and therefore only t and t' remain to be determined at the different temperatures. It was found necessary to determine t at each temperature because it does not remain constant as the temperature is changed. This change is undoubtedly due to a greater diffusion of the ions to the gauze as the temperature is raised. The value of t is greater for the negative ions than for the positive. This is what should be expected in view of the greater diffusion of the negative ions. Another effect is noticed in the case of t. As the voltage applied from the battery F is increased from zero, the current at first increases and then diminishes. The reason for this decrease of the current through the gauze is undoubtedly due to the greater number of ions drawn to the gauze at the higher voltage values. By measuring t at each temperature the method becomes independent of these changes. There are, however, several possible sources of error that must be considered. When the temperature is altered convection currents arise. Care was taken to have the vessel well surrounded by the heating or cooling medium. The metal wall of the vessel is 1.3 cm. thick, which also aids in securing uniformity of temperature. Furthermore since the field employed, 120 volts to the cm., was such as give the ions a velocity of over 100 cm. per second the convection currents present in this case can have but a small effect. Tests made under conditions most favorable for these currents seemed to show no effect. The effect of diffusion to the sides owing to the nearness of the plates is negligible.

An uncertainty enters in connection with the conditions at the gauze at the different temperatures. During the application of the reverse field the ions are driven back giving rise to a greater ionic density near the gauze which when the direct field comes on may result in a greater current through the gauze than the steady current measured by t. Also since the diffusion is different at the different temperatures the ions may not have the same starting point under all conditions. Furthermore, there is an uncertainty in connection with the potential gradient at the gauze and plate *B*. How important these considerations are is difficult to say. The method seems to give good values as compared with other methods. In the table below are given the results, in the order obtained, for the mobility of the positive and negative ions over a temperature range from − 21° C. to 63° C. The air involved in this set was dryed by passing through a tower of $CaCl_2$ and then through a specially designed drying tube immersed in liquid air. Before leaving this tube the air passed through glass wool. The chamber before filling was left evacuated for twelve hours and was also evacuated several times during filling with the dry air. The vessel, however, was not heated during the process of filling.

The pressure of the air was 73.5 cm. at 24.5° C.

Table I.

+

−184	−21	0	24	33	45	63
			1.375	1.340	1.318	1.193
			1.366	1.305	1.307	1.213
			1.334	1.333	1.208	1.216
		1.327	1.327			
		1.359				
		1.368				
		1.392	1.366			
	1.321		1.379			
	1.321					
	1.322		1.404			
1.20	1.321	1.361	1.364	1.326	1.278	1.207

−

−184	−21	0	24	33	45	63
			1.833	1.801	1.807	1.721
			1.794	1.768	1.827	1.790
			1.750	1.763	1.795	1.677
		1.602	1.707			
		1.503				
		1.495				
		1.490	1.666			
	1.638		1.576			
	1.543					
	1.607		1.524			
1.24	1.596	1.522	1.693	1.777	1.809	1.729

In Fig. 3 the average values are shown graphically by curves *A* and *B*. It is seen that the positive mobility is a maximum between the room temperatures and zero degrees. The different values are quite regular and may be repeated with fair agreement.

The negative values, however, are quite erratic. It is seen that the ratio k_-/k_+ is normal at room temperature just after filling with the dry air. As the temperature was raised the value of the mobility diminished. When the vessel had cooled to room temperature it was found that the mobility was less than the value obtained at room temperature before heating and the same effect repeated itself after each successive heating. Apparently vapor is liberated from the apparatus during heating that reduces the mobility. Upon cooling to zero there is a large decrease in the mobility. Upon further cooling the mobility is greater than at zero indicating a dryer state due to deposit of moisture on walls of vessel.

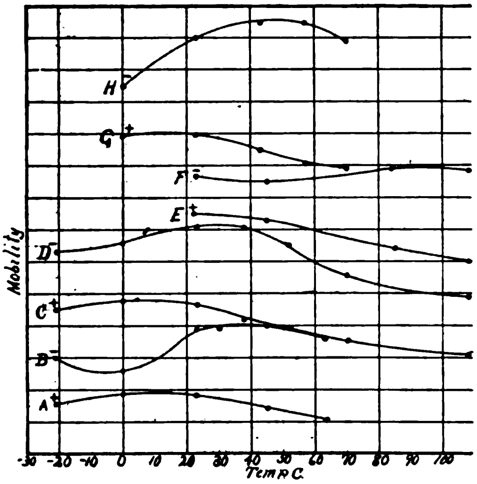

Fig. 3.

After the above readings were obtained the vessel was evacuated and kept at a temperature well over 100 C. for an hour or more. It was then evacuated filled several times while hot with air dried by passing through $CaCl_2$ and the tube immersed in liquid air. In Table II. are given the results obtained with this sample of air. The results are arranged in the order obtained beginning in each case with the value at 24° C.

These results are shown graphically in Fig. 3 by means of the curves *C* and *D*. In this case the variation of the mobility of the positive ion is quite similar to that of the preceding case except that the diminution is somewhat greater at the higher temperatures. In the case of the negative ion there is a less sudden decrease from room temperature to

Table II.

+

−21	0	24	38	52	70
		1.361	1.206	1.142	1.096
	1.365	1.330			
		1.322	1.212	1.206	
		1.331			1.107
1.30		1.327	1.209	1.178	1.101

−

−21	0	24	38°	52	70
		1.882	1.84	1.687	1.534
	1.755	1.825			
		1.812	1.78	1.716	
		1.685			1.487
1.663		1.740	1.81	1.701	1.510

zero but a greater decrease at the higher temperatures. The vessel was then evacuated and filled with air that had been allowed to bubble through water before entering the chamber. The results obtained are given in the Table III.

Table III.

+				−			
24	45	84	110	24	45	84	110
1.321				1.560			
1.326		1.12		1.592		1.625	
1.330	1.295		1.042	1.547	1.543		1.600

These results are shown graphically by means of curves *E* and *F* in Fig. 3.

It is seen that the variation of the positive mobility is in this case about the same as in the case of the drier air used in the two preceding cases. The negative shows a maximum at a higher temperature but on the whole does not vary greatly over the temperature range employed. On account of deposit of moisture on the insulation no values for zero degrees or lower were obtained.

The vessel was now evacuated and heated to about 100° C. and kept at this temperature for a period of about five hours. During this period the pump was operating constantly. A very small stream of air from a tower of $CaCl_2$ was allowed to pass through the vessel during this time. Finally the vessel was evacuated while hot, filled several times with air passed slowly through the tube immersed in liquid air.

In the Table IV. are given the results obtained in this case.

TABLE IV.

+				−			
24	43	57	70	24	43	57	70
1.398	1.287	1.206		2.032	2.094	2.080	
1.366			1.167	1.846			1.959

These results are shown graphically by means of curves *G* and *H* in Fig. 3. It is seen that the variation of the positive mobility is about the same as obtained in the preceding cases. The negative shows a marked variation and has a maximum at a higher temperature than before.

DISCUSSION OF RESULTS.

In seeking an explanation for the variation of the mobility of the positive ion the question of clustering immediately presents itself. Since, however, the mobility of the positive ion is quite independent of the presence of moisture and also since the variation with temperature is also quite independent of the condition of the air, an explanation based on clustering seems difficult. It is possible that something is driven from the wall of the vessel during heating for which the positive ion has a special attraction. It thereby becomes loaded and moves more slowly. It hardly seems probable, however, that it would unload again as the temperature is lowered; moreover this would not explain the decrease that takes place below the temperature for which the mobility is a maximum. Definite conclusion on this point will have to be postponed until a more rigid investigation has been made. The variation of the mobility of the negative ion seems to show the effect of clustering due to moisture combined with a variation similar to that observed in the case of the positive ion. Not sufficient data has been obtained, however, upon which to base any conclusion.

In connection with the observed variations an indication based on theory is of interest. Some time ago Wellish[1] suggested that the apparently large volume of the ions is due to the effect of the charge upon the mean free path, and showed that the polarization of the adjacent molecules due to the ionic charge results in an apparent increase in the radius of the sphere of action. A little later Sutherland[2] by taking into account cohesion and electrical attraction evolved the following expression for the mobility of an ion moving in a gas under the action of an electric field.

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[1] Wellish, Phil. Trans., A, Vol. 209, p. 249, January, 1909.

[2] Sutherland, Phil. Mag., 6–18, September, 1909.

$$k = \frac{e\dfrac{dE}{dx}}{\dfrac{4}{3}N_3(a_1+a_3)^2\left(\dfrac{2\pi}{3}\dfrac{m_1m_3}{m_1+m_3}m_3v_3^2\right)^{\frac{1}{2}}\left\{1+\dfrac{\varphi(a_1+a_3)+\theta(a_1+a_3)}{\dfrac{m_3v_3^2}{2}}\right\}},$$

where

N_3 = number of molecules per cm.,^{3}

$a_1 + a_3$ = the distance an ion and molecule must approach for collision,

m_1 and m_3 = mass of ion and molecule respectively,

$\varphi(a_1 + a_3)$ and $\theta(a_1 + a_3)$ are functions depending respectively upon cohesion and electric action.

By considering N_3 constant and placing

$$\frac{mv_3^2}{2} = kT,$$

where T is the absolute temperature, there results for the mobility

$$k = \frac{A\sqrt{T}}{T + C}.$$

By differentiating with respect to T and equating to zero we see that k is a maximum when $T = C$. The variation obtained, however, is greater than expressed by this equation.

SUMMARY.

The mobility of the positive and negative ions in air at atmospheric density has been measured at different temperatures by means of an alternating field method.

It was found that under the above stated conditions the mobility of the positive ion is a maximum at about 0° C. The mobility of the negative ion also shows a maximum but is more erratic in its behavior. No definite conclusion has been reached but it seems that the variation of the positive mobility is not due to clustering. The variation of the negative mobility, however, seems to be due to clustering combined with an effect similar to that causing the variation of the positive mobility.

In connection with this investigation I wish to express my thanks to Professor John Zeleny and Professor A. F. Kovarik.

Physical Laboratory,
University of Minnesota,
May, 1915.

A LENS REFRACTOMETER.

By H. F. Dawes.

THE following is a description of a convenient type of refractometer for liquids which depends on the fact that the power of a lens surface is a function of the refractive index of the substance in optical contact with it.

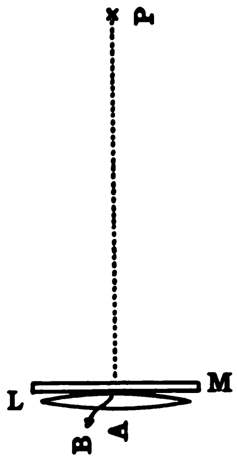

Fig. 1.

The principle of the arrangement is illustrated in Fig. 1. *L* is a double convex lens silvered on the surface *A*. *M* is a plane-parallel glass plate which touches *L* at *B*. A drop of the liquid whose index is to be found is placed between *L* and *M*. *P* is an object point so adjusted that the light which traverses the system to the silvered surface returns to form an image coincident with the original object. The position of *P* depends on the index of the liquid and may be used to find this index; the relation between the two may be found in the following way:

Notation.—Index of lens substance, n; unknown index, x; distance from *B* to *P* for adjustment described, p; radii of curvature of surfaces *A*, *B*; r, s.

The optical power of the refracting system is $(x-n)/s$. The distance, p', from *B* to the image of *P* formed by this refracting system is given by

$$\frac{n}{p'} - \frac{1}{p} = \frac{x-n}{s}.$$

Since the light must be incident normally on the surface *A* in order that it may be reflected as required, this image distance must equal the radius of curvature of *A*.

Hence $$\frac{n}{r} - \frac{1}{p} = \frac{x-n}{s}, \text{ or, } x = n\left(1 + \frac{s}{r}\right) - \frac{s}{p}.$$

In working out this relation the thicknesses of lens and plate, which are small quantities, are neglected. The more exact formula which takes these into account is

$$x = n\left(1 + \frac{s}{r-t}\right) - \frac{s}{p-t' + \dfrac{t'}{n'}},$$

(t is thickness of lens, t' is thickness and n' index of plate).

The relation is thus of the form $x = c_1 - c_2/(p - c_3)$ where the c's are constants. This comparatively simple relation makes the arrangement particularly suitable for a calibrated instrument with a scale from which the index corresponding to any setting may be read off. The calibration may be done by calculation from the above formula if the optical constants are known; otherwise a number of readings may be taken with liquids of known index and a calibration curve constructed.

Details of construction.—The object of which P is the axial point consists of the cross-hair of a collimating eye-piece, or better, a small grid ruled on glass. Image and object coincide at their axial points and are equal in size (but inverted); the advantage of the grid is that the adjustment may be assisted by testing for equality of object and image as well as for coincidence by the parallax method. The cross-hair or grid will be illuminated by the monochromatic light for which the index is required, the light being concentrated on the object by means of a small condensing lens of suitable aperture.

The tube carrying the plate M telescopes into the eye-piece tube by means of a spiral screw; by this means the distance from B to P is adjusted. The calibration scale follows the screw motion. The range of values of x required in practice extends from about 1.3 to 1.75, though it is advisable to be able to set the system for x equal to 1, *i. e.*, for air in contact with the lens).

The lens slips into place in contact with M by means of a spring clip; it may be readily removed to place a drop of the liquid under test or to clean away liquid.

The whole system, must of course, be carefully centered and the surfaces optically worked.

In a typical system the following were numerical values. Index of glass, 1.544; radii of lens surfaces 41.2 cm. each. The values of p in sodium light for air, water and glycerine were; 19.71, 23.44, 25.51 cm.

Dispersion.—It is supposed that monochromatic light is used so that the calibration scale corresponds to some selected color. If the index is required for any other color the reading must be corrected for dispersion.

To determine this correction consider the light for which the indices of glass and liquid are $n + dn$ and $x + dx$. If the refractometer is adjusted in this light the distance from P to B will be $p + dp$, given by the equation

$$x + dx = (n + dn)\left(1 + \frac{s}{r}\right) - \frac{s}{p + dp}.$$

The value of the index read off from the scale for this setting is

$$n\left(1 + \frac{s}{r}\right) - \frac{s}{p + dp}.$$

Hence the value read from the scale must be corrected by adding to it $dn\ (1 + s/r)$. Since this correction depends only on the constants of the lens it is necessary to draw up once for all a table of corrections corresponding to the different monochromatic lights available or to construct a curve showing the relation between wave-length and correction.

Sensitiveness.—The axial distance a by which object and image may be separated without showing parallax may be used to find a criterion for sensitiveness. For such a small distance of separation the correct position will lie practically midway between object and image. Hence dp the extreme error in p will be $a/2$. The corresponding error in x is dx, equal to

$$\frac{s}{p^2} \cdot dp = \frac{s}{p^2} \cdot \frac{a}{2}.$$

It appears then that the most advantageous construction is that for which p is large and s, a, small. Increase in the value of the first of these is limited, by convenience of working, to something of the order of 25 cm. so that this may be taken as a maximum value for this quantity. In considering the effect of p on the sensitiveness, it may be noted incidentally that a given instrument is more sensitive for the more highly refracting liquids since for these the values of p are larger; the calibration scale therefore becomes more open as it passes from low to high index.

The second factor, s, which enters into the sensitiveness may be diminished until the smaller aperture made necessary by the increase in curvature results in an increase in a. When the above two factors have been chosen the value of the other quantity which enters into the construction, namely, r the radius of curvature of the reflecting surface, is determined by the fundamental equation. Its value is given by substituting the selected values for p and s, the value of the index of the glass from which the lens is to be made and the maximum value of the unknown index for which the instrument is to be used.

The value of the third of the quantities affecting the sensitiveness, a, depends on the angular aperture of the pencil of light which forms the image, on the aperture and power of the eye-piece which is used to examine the image and on the resolving power of the eye itself. Under favorable conditions a may be as small as .01 cm. With this value the above limit of error in the unknown index will be .0004 for the instrument whose dimensions are given in a previous paragraph so that the value of the index may be readily obtained to better than the third decimal place. As a matter of fact the error need not be nearly so great as the above for one may obtain a more accurate value by taking the mean of the two settings for which parallax just begins to appear (*i. e.*, image distance just too great and just too small). It will be seen that the instrument is quite as sensitive as the calibrated type of total reflection refractometer.

McMaster University,
Toronto, Canada,
May 24, 1915.

A NEW FLUORESCENCE SPECTRUM OF URANYL AMMONIO-CHLORIDE.

By Edward L. Nichols and Ernest Merritt.

The spectrum of a sample of uranyl chloride (from Kahlbaum) when excited to fluorescence at the temperature of the room was measured by the present writers in 1911.[1] Like the fluorescence spectra of other uranyl salts it was found to consist of a series of nearly equidistant bands extending from the red to the blue. The crests of the six brightest bands, according to our observations, were at .5928μ, .5631μ, .5369μ, .5121μ, .4950μ, and .4769μ. At low temperatures this spectrum, which is comparatively feeble at + 20°, is resolved into a complex of very narrow bands similar to those described,[2] in the case of the other uranyl salts, by J. Becquerel and Onnes.

In the preparation of uranyl compounds, undertaken for us in the chemical laboratory of Cornell University by Mr. G. O. Cragwell a uranyl salt was obtained in the form of tri-clinic crystalline plates which we have since found to have the composition $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$.

These crystals are strongly fluorescent, and the fluorescence spectrum, unlike that of the other uranyl salts thus far described, is resolved at room temperature into at least eight groups of narrow bands. Each group, which corresponds to a single band of the ordinary uranyl fluorescence spectrum, consists of five nearly equidistant bands.

The symmetry of this spectrum, as it appears to the eye when viewed with a spectroscope of moderate dispersion, is most striking. While not so narrow as some of the line-like bands of uranyl spectra when excited at the temperature of liquid air, the bands are well separated from their neighbors and are about 18 Ångström units in width or one tenth as wide as the bands of the ordinary type of the uranyl fluorescence spectrum at + 20° C. Each group of five, indeed, occupies approximately the same space in the spectrum as an ordinary single band.

The distribution of intensities within the group was determined for the visually brightest group (.5302 ··· .5114), by means of the spectrophotometer. The results are given in Table I. and are shown graphically in Fig. 1.

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[1] Nichols and Merritt, Phys. Rev. (1), XXXIII., p. 355.

[2] J. Becquerel and Onnes, Leiden Communications, 110, 1909.

TABLE I.

Intensities of Bands in Group 6. (Excited at + 20°.)

Band.	Intensity.
.5302μ	18
.5253	33
.5203	24
.5157	11
.5114	[1]

[1] Visible but too dim for spectrophotometric measurement.

The curve (Fig. 1) which forms an envelope of the group of bands is of the same type as that for the distribution of intensities in a single band of the ordinary uranyl fluorescence spectrum and of the envelope of the set of bands in such a spectrum and is also similar to curves of distribution of the fluorescent spectra having a single broad band, such as resorufin.[1]

The effect of cooling is likewise analogous, the envelope for − 185° being narrower on account of the great relative reduction in brightness of the outlying members of the group. All the bands are shifted in position as well as changed in intensity in a manner to be described in a subsequent paragraph.

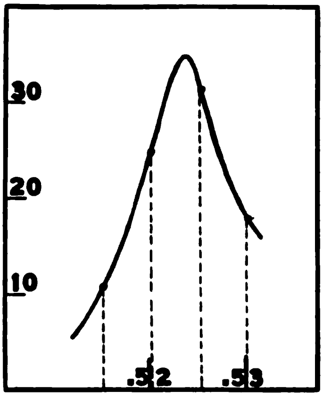

Fig. 1.

To determine as closely as possible the wave-lengths of the bands, photographs of the spectrum were taken. Fluorescence was excited by means of the carbon arc, the light from which passed through a screen opaque to rays of wave-length greater than about .45μ and was focused upon the crystal. Various exposures were employed on account of the great differences in the intensity of the bands and special plates were used for the red end of the spectrum. The exciting light was excluded from the camera by the use of suitable screens opaque to the blue and violet except where the absorption spectrum was to be recorded.

The various negatives were measured by mounting them on a micrometer stage in the field of the lantern. The micrometer screw was carefully calibrated so that wave-lengths could be determined by measuring the distance of the crests of the bands from certain reference lines of the mercury spectrum which was photographed on each negative so as to overlap the fluorescence spectrum.

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[1] Nichols and Merritt, *l. c.*

This method of projection was found better than the use of the comparator commonly employed in the measurement of line spectra, because of the hazy character of the bands and because bands that are so weak and vague as to be invisible even under a low power microscope could be seen and located by means of the lantern. Many measurements of the stronger bands were made with comparator as a check on the determinations with the lantern.

The results of these measurements confirmed to a remarkable degree the apparent symmetry of the spectrum. When all the bands are plotted on a large scale, in a diagram with the reciprocal of wave-lengths as abscissae, the spectrum is seen to consist of eight groups of five bands each as already described. The bands of each group are very nearly equidistant, and corresponding members of the groups form an homologous series of equidistant bands. This interval moreover is very nearly the same for all five of these homologous series; but although the departures from equality are of the same order as the errors of measurement there is strong reason to regard them as real. Finally the groups taken as units and counting from their centers (obtained by averaging the frequencies of the bands in each) are equally distant within the errors of measurement.

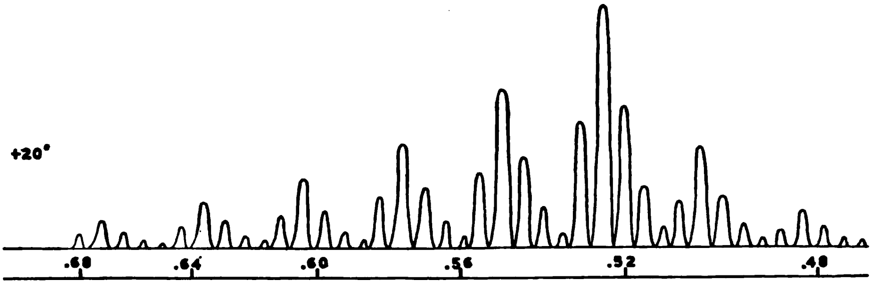

Fig. 2.

The location of the various bands, as determined from the photographs, are given in Table II. The positions of the bands and their relative intensity, as estimated by the eye, are shown in Fig. 2. Horizontal distances are plotted on the scale of frequencies, the corresponding wavelengths being indicated for convenience. In group 1, which lies in the red, band *e* is missing while in group 8 only the strongest band (*c*) was visible in any of the photographs.

This spectrum approximates very closely, *i. e.*, in most cases within or almost within the errors of observation, to a series of equidistant groups each consisting of five equidistant bands; distance being expressed in frequency. Were this strictly true the frequency interval of the

Table II.

Observed Positions of Bands at + 20°.

Group.	Band.	λ	$1/\lambda \times 10^3$	Group.	Band.	λ	$1/\lambda \times 10^3$
1	*b*	.6804	1,469.7	5	*b*	.5547	1,802.8
	c	.6711	1,489.9		*c*	.5493	1,820.5
	d	.6635	1,507.1		*d*	.5437	1,839.4
	e	.6585	1,521.8[1]		*e*	.5387	1,856.0
	a	.6501	1,538.2		*a*	.5344	1,871.2
2	*b*	.6438	1,553.3	6	*b*	.5302	1,886.1
	c	.6356	1,573.4		*c*	.5252	1,904.0
	d	.6293	1,588.9		*d*	.5201	1,922.6
	e	.6230	1,605.1		*e*	.5157	1,939.2
	a	.6167	1,621.5		*a*	.5114	1,955.3
3	*b*	.6101	1,638.9	7	*b*	.5076	1,970.1
	c	.6039	1,655.9		*c*	.5035	1,986.2
	d	.5978	1,672.8		*d*	.4986	2,005.7
	e	.5919	1,889.4		*e*	.4944	2,022.6
	a	.5862	1,705.9		*a*	.4906	2,038.3
4	*b*	.5814	1,719.9	8	*b*	.4870	2,053.3[1]
	c	.5751	1,738.7		*c*	.4828	2,071.0
	d	.5697	1,755.4		*d*	.4787	2,089.0[1]
	e	.5643	1,772.2		*e*	.4749	2,105.9[1]
	a	.5589	1,789.1		*a*	.4714	2,121.5[1]

homologous series of bands, *b*, *c*, *d*, *e* and *a* would be the same, and for each uniform throughout the spectrum and this interval would be the same as that between the successive groups taken as a whole. Finally the distances between neighboring bands would be the same within each group and for each group.

To test the intervals between groups the position of what may be called the center of each group was found by averaging the frequencies of all five bands and the intervals between these average positions for groups 2, 3, 4, 5, 6 and 7 were found.

Groups 1 and 8, for which insufficient data were available, were omitted.

The results are given in the tables III and IV.

The departures from uniformity in the intervals between groups (Table III.) are of the same order as the errors of observation and there is no indication of a progressive or systematic change. We may conclude therefore that within the accuracy of these measurements, *the groups are equidistant.*

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[1] Band *e* (group 1) and bands *b*, *d*, *e* and *a* (group 8), which were indistinguishable in the photographs, have been assigned positions on the assumption of complete symmetry throughout the spectrum.

TABLE III.

Distance Between Groups.		
Group.	**Center.**	**Intervals.**
2	1,588.8	
3	1,671.7	82.96
4	1,754.6	82.86
5	1,837.8	83.20
6	1,921.2	83.40
7	2,003.9	82.76

TABLE IV.

Distance Between Neighboring Bands (Average).		
Band.	**Center of Series.**	**Intervals.**
b	1,762.1	
c	1,779.9	17.86
d	1,797.6	17.73
e	1,814.1	16.49
a	1,830.1	16.01

In a similar manner averages were found for the frequencies of each of the sets of homologous bands (*b*, *c*, *d*, *e*, *a*), and these form a group of averages, not coinciding with any actual group in the spectrum, the distances between the bands of which should however represent the mean distances of neighboring bands more closely than do the actual distances in any single group taken separately.

These averages are given in Table IV. from which it appears that the bands are not distributed uniformly within the group but that the distance between them *diminishes progressively as we pass towards the violet.* The distance between the last band (*a*) of any group and the first (*b*) of the next group is so nearly equal to the distances between the bands within the group that it was difficult, before the completion of these computations, to decide as to the boundaries between the groups. The casual appearance of the spectrum as may be seen from Fig. 2 is that of a succession of equidistant bands varying periodically in intensity. It was at first thought that the crest band (*c*) of each group formed the center with two weaker bands on either side and band (*a*) was supposed to be the first in each group counting from red towards violet. This designation has not been altered although it was found by measurement that band *a* in each group was distinctly nearer to band *b* (average distance 14.4) than to band *e* and should be considered as the last band of the group.

The Detailed Study of the Intervals of the Several Homologous Series of Bands (*b*, *c*, *d*, *e*, *a*).

To compare the intervals between homologous bands these were averaged for each series separately by the method of subtracting the frequency of each band of the series from the member of greater frequency and dividing the sum by the total number of intervals. The averages thus computed are as follows:

Table V.

Average Intervals between Homologous Bands.

Series.	Interval.
b (7 members)	83.19
c (8 members)	82.80
d (7 members)	83.25
e (6 members)	83.42
a (7 members)	83.26
General average,	83.20

For homologous series *b*, *d*, *e* and *a* the average distance between bands is the same within the errors of observation and approximately equal to the distance between the various groups considered as units. The interval for series *c* is smaller than for the other series and the difference, while scarcely larger than might be accounted for by experimental errors, appears to be a real one, appearing consistently in all the photographs taken of this spectrum and likewise in the case of spectrophotometric observations made to check the photographic determinations. To ascertain whether the groups of bands as individually measured really conformed to the description suggested in an earlier paragraph of a system of equidistant groups consisting of five homologous series of equidistant bands having a common interval, the positions of the members of a hypothetical system of this sort were computed in the following manner and the individual departures of the actual bands were determined.

It was assumed that the measurements of series *c* were slightly at fault and that the proper interval for the entire system was the average for the other four series, *i. e.*, 83.25. Using this interval the hypothetical bands were located about the "center" of each series and their positions were compared with those of the corresponding actual bands.

The results are shown in the following table in which the frequencies of the hypothetical bands are given in the columns marked "calculated," those of the actual bands in the columns marked "observed" and departures in those marked "differences."

The Effect of Temperature.

Ordinarily, when a uranyl salt is cooled to the temperature of liquid air the series of equidistant bands of its fluorescence spectrum, each of which corresponds to one of the eight groups of five narrower bands already described in the case of this form of uranyl ammonio-chloride, is resolved into a rather complex aggregation of narrow line-like bands.[1]

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[1] See H. Becquerel, Comptes Rendus, 144, p. 671; also J. Becquerel and Onnes, Leiden Communications, No. 110, 1909.

TABLE VI.

Calculated and Observed Frequencies of the Various Series of Bands.

Series.	Group.	Calculated.	Observed.	Differences.	Intervals.
b	1	1,470.3	1,469.8	+ .5	
	2	1,553.6	1,553.3	+ .3	83.60
	3	1,636.8	1,638.9	−2.1	85.60
	4	1,720.1	1,719.9	+ .2	81.00
	5	1,803.3	1,802.8	+ .5	82.95
	6	1,886.6	1,886.1	+ .5	83.30
	7	1,969.8	1,970.1	− .3	83.95
	8	2,053.1			
c	1	1,488.6	1,489.9	−1.3	
	2	1,571.8	1,573.4	−1.6	83.55
	3	1,655.1	1,655.9	− .8	82.45
	4	1,738.3	1,738.7	− .4	82.85
	5	1,821.5	1,820.5	+1.0	81.80
	6	1,904.7	1,904.0	+ .7	83.50
	7	1,988.0	1,986.2	+1.8	82.25
	8	2,071.2	2,071.0	+ .2	84.85
d	1	1,506.2	1,507.1	− .9	
	2	1,589.5	1,588.9	+ .6	81.80
	3	1,672.7	1,672.8	− .1	83.90
	4	1,756.0	1,755.4	+ .6	82.65
	5	1,839.2	1,839.4	− .2	84.00
	6	1,922.5	1,922.6	− .1	83.15
	7	2,005.7	2,005.7	0	83.15
	8	2,089.0			
e	1	1,522.7			
	2	1,605.9	1,605.1	+ .8	
	3	1,689.2	1,689.4	− .2	84.10
	4	1,772.4	1,772.2	+ .2	82.85
	5	1,855.7	1,856.0	− .3	83.75
	6	1,938.9	1,939.2	− .3	83.20
	7	2,022.2	2,022.6	− .4	83.45
	8	2,105.4			
a	1	1,538.7	1,538.2	+ .5	
	2	1,622.0	1,621.5	+ .5	83.25
	3	1,705.2	1,705.9	− .7	84.40
	4	1,788.5	1,789.1	− .6	83.20
	5	1,871.7	1,871.2	+ .5	82.20
	6	1,955.0	1,955.3	− .3	84.10
	7	2,038.2	2,038.3	− .1	83.00
	8	2,121.4			

It was deemed of interest to determine the effect of temperature on a spectrum which was already at least partially resolved at + 20° and for this purpose the ammonio-chloride under consideration in the present paper was subjected to cooling. Visual measurements of such of the bands as could be determined in this way were made at + 20°, 0°, − 30°, − 60°, − 90°, − 120°, − 150° and − 180°. Several sets of photographs of the spectrum were likewise obtained with the substance excited at − 185°.

When the substance, excited to fluorescence in the manner already described, was gradually cooled to the temperature of liquid air and as the spectrum was observed through the Hilger spectrometer the following changes were noted:

1. The bands become narrower and better defined until at the temperature of liquid air they correspond in appearance to the usual line like bands characteristic of the fluorescence spectra of the uranyl salts at low temperatures.

2. There is a shift towards the violet *amounting to more than a third of the distance between the bands.*

3. The following new bands appear: At about − 25° a very narrow band between *c* and *d* of each group; feeble at first but increasing in brightness with falling temperature. At about − 90° the *c* bands begin to appear double or in other words a new set becomes visible between *c* and *b*. At about − 150° another set of bands becomes visible between *e* and *a*.

Were the shift noted above the same for the different bands in each group and throughout all the groups, the spectrum at − 185°, at least as to the series, *b*, *c*, *d* and *e*, which are visible at both temperatures, would be located throughout by applying the mean observed shift to all the bands of the spectrum at + 20°.

The nature of the shift which these bands undergo appears to be as follows:

Each band may be regarded as an unresolved doublet, of which in general the member of longer wave-length is relatively so much the stronger that its position determines approximately the location of the crest of the composite band (see Fig. 3). The effect of cooling is to resolve this doublet into separately distinguishable bands and at the same time to cause a subsidence of the stronger and an increase of the weaker member. The member of shorter wave-length becomes dominant at low temperatures in each doublet and the arrangement of the entire spectrum therefore appears to be undisturbed but shifted towards the violet by an amount representing the width of the doublet.

Since however the doublet is now resolved by the narrowing of the components we might expect to be able to distinguish the original member of longer wave-length unless by cooling it has disappeared altogether. The appearance of the group, if this be its real structure (*i. e.*, a set of equidistant doublets, the distance between the members of all the doublets being nearly the same) would then be as shown in the lower part of Fig. 3 (− 185°).

At + 20° *b'*, *c'*, *d'*, *e'* and *a'* are entirely concealed by the overlapping of the bands. At − 185° *b*, *c*, *d*, *e* and *a* may or may not be visible according to their intensity or to the completeness of the resolution which in fact differs greatly in different portions of the spectrum. At − 185° however *b*, *c*, *d*, *e* and *a* being very weak as compared with *b'*, *c'*, *d'*, *e'* and *a'* or in some cases almost invisible, the appearance is that of a shift equal to the distance *bb'*, *cc'*, etc.

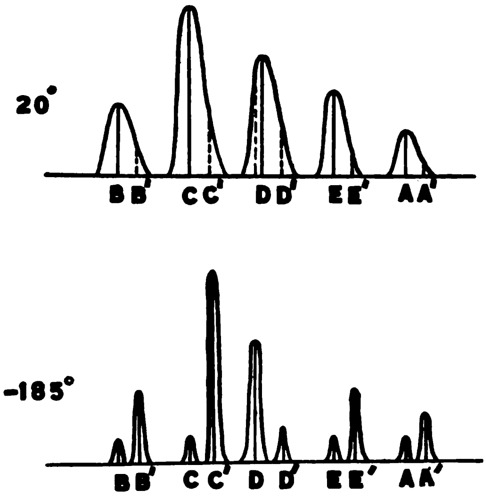

Fig. 3.

TABLE VII.

Shift of the c Series Between + 20° and − 185° C.

1/(*Observed.*)

Series.	Group.	+ 20°.	− 185°.	Shift.
c	1	1,489.9	1,496.5	6.6
	2	1,573.4	1,579.8	6.4
	3	1,655.9	1,662.1	6.2
	4	1,738.7	1,744.4	5.7
	5	1,820.5	1,827.7	7.2
	6	1,904.0	1,910.6	6.6
	7	1,986.2	1,992.7	6.5
	8	2,071.6	———	——
			Average,	6.5

When we apply this test, making use of the photographic measurements at − 185°, we find for series *c* a shift that is uniform throughout the spectrum, see Table VII.

It follows, obviously, that the interval for the *c* series is the same, within the errors of observation, at − 185° and at + 20°. The actual averages from observed positions are respectively: 82.8 (+ 20°) and 82.5 (− 185°).

For the *b* series we obtain likewise a constant shift except in the extreme red (groups 1 and 2) where the bands are so faint as to be almost indistinguishable and the resolution is imperfect so that the vague bands on the negatives are probably composite (see Table VIII.).

TABLE VIII.

Shift of the b Series Between + 20° and − 185° C.

1/(*Observed.*)

Series.	Group.	+20°.	−185°.	Shift.
b	1	1,469.7	1,479.7(?)	10.0(?)
	2	1,553.3	1,563.0(?)	9.7(?)
	3	1,638.9	1,645.0	6.1
	4	1,719.9	1,726.9	7.0
	5	1,802.8	1,810.4	7.6
	6	1,886.1	1,894.4	8.3
	7	1,970.1	1,977.9	7.8
	8	———	———	——
		Average (omitting groups 1 and 2), 7.7		

In the case of the *d* series the effect of the lack of resolution in the red end of the spectrum is more clearly marked and is capable of definite description. Here we find the bands of groups 4, 5, 6 and 7 in their expected places and showing the proper shift (see Table IX.), whereas

TABLE IX.

Shift of the d Series Between + 20° and − 185° C.

1/(*Observed.*)

Series.	Group.	+20°.	−185°.	Shift.
d	1	1,507.1	1,508.9	1.8
	2	1,588.9	1,591.5	2.6
	3	1,672.8	1,675.6	2.8
	4	1,755.4	1,761.4	6.0
	5	1,839.4	1,845.1	5.7
	6	1,922.6	1,929.2	6.6
	7	2,005.7	2,013.4	7.7
	8	———	2,097.1	——
			Average (groups 4 to 8), 6.5	

Average interval at +20° = 83.24

Average interval (groups 4 to 8) at −185° = 83.93

in groups 1, 2 and 3 they are considerably displaced towards the violet having a position intermediate between the places which the band *d* and the new intermediate bands should occupy. In other words in these groups of longer wave-length, these bands, which in the remainder of the spectrum are separate and well defined, are not resolved.

The interpretation of the changes occurring in the regions of the spectrum occupied by the *d*, *e* and *a* bands is most readily studied by means of the diagram in Fig. 4, in which the bands of each group at − 185° are shown in their relation to a hypothetical grouping given at the head of the column. This grouping consists of the set of imagined doublets of which as in a previous paragraph the spectrum at + 20° was supposed to be made up. The spacing for each doublet is that determined from the observed shift on cooling and the relative divergence from this arrangement is shown for all the bands of each group.

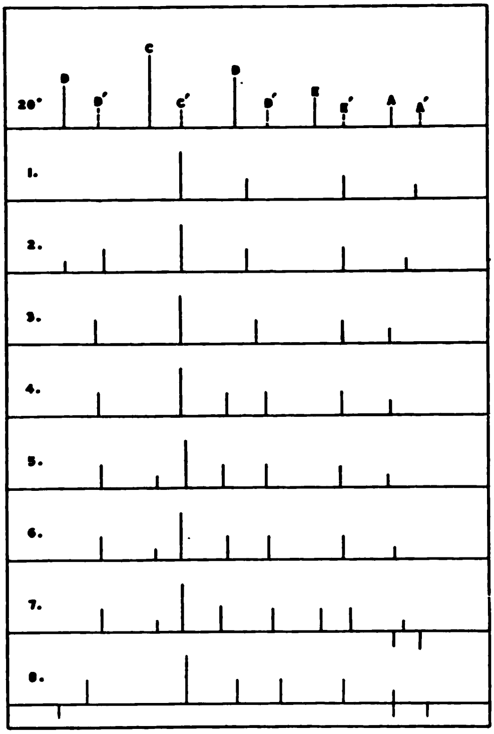

Fig. 4.

A scrutiny of the fluorescence spectrum at − 185° group by group, by means of this diagram, affords very satisfactory confirmation of this hypothesis concerning the apparent shift. It is obvious:

1. That not all the components *b*, *c*, *d*, *e* and *a* will necessarily be visible in every group of the resolved spectrum:

2. That lack of resolution in any region may give the appearance of a single band with intermediate crest in place of the doublet:

3. That the position of crests of the unresolved doublets at + 20° will not necessarily coincide exactly with that of either component.

Bearing these points in mind, it will be seen that were resolution complete all the oserved bands of the spectrum at − 185° would probably fall into the system proposed above.

We may imagine that the difference between the resolution of the bands *c* and *d*, for example as seen in Fig. 4, is produced by changes in the unresolved doublets at + 20° when the temperature is reduced to − 185°, of the kind indicated in Fig. 5. The doublet *cc′* forms a single band with crest nearly coincident with *c* at + 20° and this owing to the subsidence of *c* and growth of *c′* takes the resolved form shown at − 185°. In the case of *d* however the unresolved band has an intermediate crest at *d* but is really composed of overlapping components *d′* and *d″* which are separately visible at − 185°.

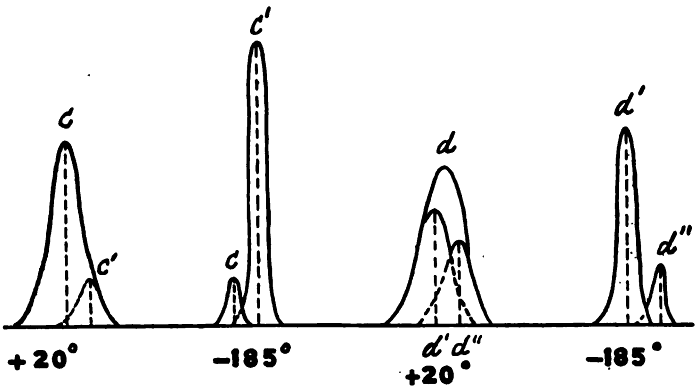

Fig. 5.

The Absorption Spectrum.

The absorption spectrum of this salt of which observations were made both visually and photographically likewise consists of several series of equidistant bands having a common interval.

Fluorescence and absorption overlap as in the case with all the uranyl spectra thus far studied, and one group of bands (group 7 of the fluorescence spectrum) which we have called the *reversing group* is common to both spectra. The bands of this group may be made to appear either as fluorescence bands or as absorption bands according to the conditions of the experiment. The reversal may be effected by the simple expedient of varying the character of the incident light. With a screen which extinguishes the yellow and green and transmits shorter wave-lengths the fluorescence bands of this region appear on a dark background. With a yellow screen that reduces excitation to a minimum, absorption bands are seen to take their place. These, in general, coincide in position with the fluorescence they displace, but since as has been shown the bands are doublets of unequal brightness an apparent shift sometimes occurs.

The weaker band of the fluorescence pair becomes the stronger in the absorption spectrum as illustrated in Fig. 6, which is from a photograph of such a doublet when emitting and when absorbing light. In such cases the weaker bands are often invisible unless special precautions are taken to bring them out and there is an apparent shift equal to the distance between the members of the doublet.

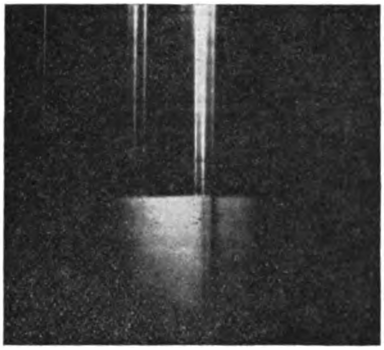

Fig. 6.

Since the temperature shift in the bands of the fluorescence spectrum, as stated in a previous paragraph, is mainly due to the subsidence of the stronger and the "crudescence"of the weaker member of such doublets, upon cooling to the temperature of liquid air we should expect the location of the absorption bands when thus displaced at room temperature to coincide with the low temperature positions of fluorescence, and this is found to be the case in many instances.

Unfortunately the complete analysis of the absorption spectrum is rendered difficult, not only by the varying degrees of resolution, as in the case of the fluorescence bands, but also by the existence of a general absorption which increases rapidly towards the violet and renders the crystals almost opaque to the violet and ultraviolet rays.

The absorption spectrum at + 20° extends from the reversing region into the ultraviolet.

It consists of the following series:

1. $\beta\alpha$; so designated because its first member at .5076μ ($1/\lambda \times 10^3$

= 1,970) is coincident with and a reversal of the *b* band in that group, while its second member at .4899μ ($1/\lambda \times 10^3 = 2{,}041$) is so nearly coincident with the *a* band of the same group that it may be supposed to form a close and unresolved doublet with the absorption series related to that band.

2. γ; having its first member at .5028μ ($1/\lambda \times 10^3 = 1{,}989$) and the reversal of the *c* band in that group.

3. δ′ and δ; two series, having their origin on either side of the *d* band; as if this band were a doublet, unresolved in the fluorescence but resolved in portions of the absorption spectrum.

4. ε and ε′; two series, one of which ε begins as the reversal of the *e* band at .4942 ($1/\lambda \times 10^3 = 2{,}023$) while the companion series ε′, which possibly belongs to an unresolved component of the *e* band, first becomes distinguishable as a faint absorption band at 2,173.

The constant frequency interval common to all these series is approximately 71[1] instead of 83.2 which is the average interval for the fluorescence bands. This sudden break to a shorter interval in passing from fluorescence to absorption is not new. It is characteristic of all absorption spectra of the uranyl salts thus far studied at room temperature[1] and corresponds, approximately, with the intervals between the absorption bands of solutions of these salts given by Jones and Strong.[2] We have tried in vain not only in the case of the chloride but likewise with the

TABLE X.

Relation Between Absorption bands of UO_2Cl_2 *in Solution* (.49μ *to* .67μ) *and the* α, γ, δ *and* ε *Series.*

UO_2Cl_2 in H_2O Jones and Strong.		Corresponding Series of $2NH_4Cl.UO_2Cl_2+2H_2O$ (Crystals).	
λ	$1/\lambda \times 10^3$	Series.	$1/\lambda \times 10^3$ (Computed).
.6700	1,492	γ	1,492
.6500	1,538	α	1,544
.6300	1,587	δ	1,583
.6070	1,647	δ′	1,646
.6040	1,656	δ	1,653
.6020	1,661	–	——
.6000	1,667	ε	1,668
.5480	1,825	α	1,828
.5200	1,923	–	——
.5185	1,929	δ′	1,930
.4900	2,041	α	2,041

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[1] See Nichols and Merritt, Phys. Rev., Vol. 33, p. 354.

[1] The actual observed range, as will be seen from Table XI., is from 70.4 for series γ to 71.5 for series *βα*, and these differences are presumably due to the varying relations of the unresolved components of the doublets of which the bands are composed.

[2] Jones and Strong, Publications of the Carnegie Institution, No. 130, p. 89, also Physikalische Zeitschrift, 10, p. 497.

crystals of the nitrate and with other solid uranyl salts, to trace the absorption into the realm of the fluorescence spectrum. Jones and Strong, however, working with solutions of uranyl chloride in water, have located various absorption bands of longer wave-lengths.

TABLE XI.

"Absorption" Bands of $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$ *at* + 20° *C. Arranged in Series.*

Series $\beta\alpha$.			Series γ.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
5,076	1,970.1	71.5	5,029	1,988.5	70.4
4,899	2,041.2		4,860	2,057.5	
4,733	2,113.0		4,704	2,126.0	
4,577	2,185.0		——	——	
4,433	2,256.2		——	——	
4,293	2,329.5		——	——	
4,166	2,400.3		——	——	
——	——		——	——	
——	——		——	——	
——	——[1]		3,815	2,620.9	
——	——[1]		3,714	2,692.8	
3,627	2 756.8		——	——	
Series δ'.			**Series δ.**		
4,996	2,001.6	70.7	4,978	2,008.9	70.5
4,829	2,070.6		4,908	2,080.1	
4,667	2,142.6		4,652	2,149.5	
——	——		4,507	2,218.9	
——	——		4,370	2,288.5	
——	——		4,237	2,359.9	
——	——		4,112	2,432.0	
——	——		3,997	2,501.8	
3,898	2,565.1		3,885	2,573.7	
3,792	2,637.1		——	——	
3,692	2,708.6		3,685	2,713.7	
Series ϵ.			**Series ϵ'.**		
4,942	2,023.3	70.9	——	——	71.0
4,776	2,094.0		——	——	
4,618	2,165.5		4,601	2,173.5	
——	——		4,455	2,244.5	
4,331	2,309.0		4,320	2,314.6	
4,202	2,379.9		4,194	2,384.6	
——	——		4,073	2,455.2	
——	——		3,957	2,527.4	
3,863	2,588.7		——	——	
3,757	2,661.7		——	——	
——	——		3,648	2,741.2	

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[1] Two bands at 2,604.6 and 2,675.2 are perhaps to be regarded as members of this series but displaced about 10 to the red. They are designated as α'.

We were surprised to find that of eleven bands indicated by them as lying between .4900μ and .6700μ nine might be considered as related to the various series described in the present paper. In the following table the wave-lengths and frequencies of these bands are given together with the frequency of the corresponding member of our series computed on the assumption of its extension towards the red with the constant interval of 71.

Considering that the bands of Jones and Strong are for the simple chloride in solution, it might be held that a comparison with bands of a double chloride in the crystalline form is entirely without significance. It has seemed worth while however to call attention to these approximate coincidences of position.

Table XI. gives the bands thus far located in the absorption spectrum at + 20° C. It will be noted that series γ and δ' disappear after the third member but reappear in the extreme violet; also that δ, which appears as a doublet with δ' at both ends of the spectrum, continues throughout the wide gap between .47μ and .39μ where γ and δ' are missing.

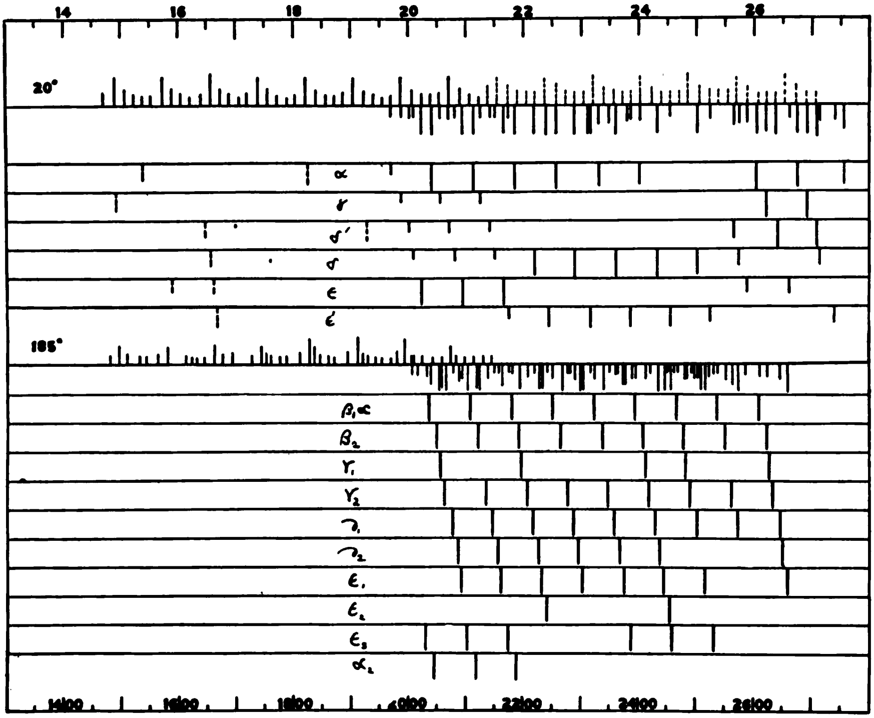

Fig. 7.

The absorption spectrum of this salt at − 185° undergoes changes strictly analogous to those described in the case of the fluorescence spectrum. There is the usual narrowing of the bands with further resolution. The bands in the absorption spectrum however are still capable of arrangement in series with a nearly constant frequency interval of about 71 and these series in general have their origin in coincidence with a fluorescence series. The apparent exceptions are undoubtedly due to the fact that the bands, both of fluorescence and absorption, are complex and only partially resolved.

The general grouping of the fluorescence and absorption bands at

TABLE XII.

"Fluorescence" Bands of $UO_2Cl_2\cdot 2NH_4Cl + 2H_2O$ *at* − 185° *C. Arranged in Series.*

Series b_1.			Series b_2.		
λ	$1/\lambda \times 10^8$	Average Interval.	λ	$1/\lambda \times 10^8$	Average Interval.
——	——	83.0	6,758	1,479.7	83.2
——	——		6,398	1,563.0	
6,110	1,636.7		6,079	1,645.0	
——	——		5,791	1,726.9	
——	——		5,524	1,810.4	
——	——		5,279	1,894.4	
5,080	1,968.7		5,056	1,977.9	
Series c.			Series d_1.		
6,682	1,496.5	82.6	——	——	83.8
6,330	1,579.8		——	——	
6,016	1,662.1		——	——	
5,733	1,744.4		5,704	1,753.1	
5,471	1,827.7		5,445	1,836.7	
5,234	1,910.6		5,206	1,921.0	
5,018	1,992.7		4,989	2,004.5	
Series d_2.			Series e_1.		
6,628	1,508.9	84.2	——	——	82.4
6,283	1,591.5		——	——	
5,968	1,675.6		——	——	
5,677	1,761.4		——	——	
5,420	1,845.1		5,379	1,859.0	
5,184	1,929.2		5,149	1,941.9	
4,967	2,013.4		4,940	2,024.1	
Series e_2.			Series a.		
6,538	1,529.6	83.3	——	——	83.1
6,207	1,611.0		——	——	
5,899	1,695.0		——	——	
5,624	1,778.1		5,595	1,787.3	
5,370	1,862.0		5,345	1,870.8	
5,141	1,945.0		5,118	1,953.7	

Table XIII.

Absorption Bands of $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$ *at* − 185° *C. Arranged in Series.*

Series β_{1a}.			Series β_2.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
4,906	2,038.5	71.2	4,875	2,051.1	71.5
4,742	2,109.0		4,711	2,122.7	
4,587	2,180.2		4,560	2,193.1	
4,443	2,250.9		4,413	2,265.9	
4,305	2,322.8		4,277	2,338.2	
4,177	2,394.0		4,152	2,408.7	
4,054	2,466.8		4,034	2,479.0	
3,941	2,537.3		3,922	2,550.1	
3,833	2,609.0		3,813	2,622.7	
Series γ_1.			Series γ_2.		
4,863	2,056.5	71.5	4,843	2,064.7	71.1
—	—		4,680	2,136.5	
4,551	2,197.3		4,530	2,207.3	
—	—		4,389	2,278.3	
—	—		4,259	2,348.1	
4,146	2,411.9		4,134	2,419.0	
4,028	2,482.5		4,016	2,489.9	
—	—		3,904	2,561.6	
3,808	2,626.3		3,798	2,633.0	
Series δ_1.			Series δ_2.		
4,813	2,077.9	71.0	4,792	2,086.8	70.5
4,654	2,148.9		4,639	2,155.5	
4,508	2,218.2		4,490	2,227.0	
4,370	2,288.5		4,352	2,298.0	
4,239	2,359.1		4,222	2,368.3	
4,114	2,430.9		4,102	2,437.9	
3,997	2,502.0		—	—	
3,886	2,573.2		—	—	
3,780	2,645.5		3,774	2,650.0	
Series ϵ_1.			Series ϵ_2.		
4,778	2,092.7	70.7	—	—	70.9
4,625	2,162.1		—	—	
4,478	2,233.0		4,460	2,242.2	
4,341	2,303.4		—	—	
4,209	2,376.0		—	—	
4,090	2,445.0		4,073	2,454.9	
3,975	2,515.8		—	—	
—	—		—	—	
3,763	2,657.5		—	—	

TABLE XIII.—*Continued.*

Series e_3.			Series a_2.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
4,924	2,031.0		4,889	2,045.5	
4,756	2,102.4		4,724	2,116.9	
4,599	2,174.4		4,571	2,187.7	
——	——		——	——	
——	——	71.4	——	——	71.0
4,188	2,387.5		——	——	
4,066	2,459.7		——	——	
3,951	2,530.7		——	——	
——	——		——	——	

+ 20° and – 185° is shown in Fig. 7 and the bands, arranged by series as determined from the observations at – 185° are given in Tables XII. and XIII. The different series in the absorption spectrum also shown graphically in Fig. 7. The dotted lines in the upper portion of this figure show the positions in which we should expect fluorescence bands to be found if the fluorescence had extended into the violet.

In a recent paper[1] it has been shown that the fluorescence and absorption of these crystals consists throughout of doublets polarized at right angles to each other and unresolved when the spectrum is observed without the aid of a Nicol prism or other analyzer. These polarized spectra and their relation to those described here will be considered in detail in a forthcoming article.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
June 2, 1915.

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[1] Nichols and Howes, Proceedings of the National Academy of Sciences, Vol. 1, p. 444.

THE VARIATION OF THE SPECIFIC HEAT OF SOLIDS WITH TEMPERATURE.

By Arthur H. Compton.

THE very considerable success of the quantum hypothesis in explaining the variations of the specific heat of solids with temperature has been taken as a strong confirmation of that hypothesis. Before this evidence can be considered as conclusive, however, it is necessary to see if there may not be some other satisfactory solution of the problem of specific heat, which does not involve the conception of quanta. It has been pointed out by several writers[1] that the sharp decrease of the specific heat of solids at low temperatures can be qualitatively explained if it is assumed that at these temperatures the atoms become so intimately associated that degrees of freedom are lost. In fact Benedicks[1] has been able to obtain an empirical expression on this assumption which, with properly chosen constants, fits the experimental data acceptably. In the present paper an assumption is introduced which leads directly to an expression for the variation of the specific heat with temperature which will be shown to agree at least as well with experiment as the expressions derived from the quantum hypothesis.

The assumption on which the following work is based is:

If the relative energy between two neighboring atoms in a solid falls below a certain critical value, the two atoms become agglomerated[2] so that the degree of freedom between them vanishes; but as soon as the energy increases again above the critical value, the degree of freedom reappears.

The defence of this assumption from various lines of evidence will form the subject of a later paper.

Derivation of a Formula for the Specific Heat.

The energy content of the unagglomerated degrees of freedom may be written, according to equipartition,

$$U_u = nRT,$$

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[1] F. Richarz, Zeitschr. f. anorg. Chem., 58, 356; 59, 146. J. Duclaux, Compt. Rend., 155, 1015. C. Benedicks, Ann. d. Phys., 42, 133.

[2] The term "agglomeration," suggested by Benedicks, is used to indicate any state of association of the atoms on account of which degrees of freedom for thermal motion disappear.

where n is the number of unagglomerated degrees of freedom, R the gas constant for a single molecule, and T the absolute temperature. In the case of the chemical combination of two atoms, when a degree of freedom vanishes its energy is usually transmitted to the other degrees of freedom in the form of heat of formation. In the case of endothermic substances, however, the vanishing degree of freedom absorbs a certain amount of energy. We may assume provisionally, therefore, that when two atoms in a solid agglomerate they retain a certain amount of potential energy. The amount of this energy will be,

$$U_a = \gamma(3N - n),$$

where γ is the potential energy of each agglomerated degree of freedom, and $3N$ is the greatest possible number of degrees of freedom. The total energy content of the solid is therefore,

$$U = U_u + U_a = nRT + \gamma(3N - n).$$

If we call P the probability that a certain possible degree of freedom shall actually exist, $P = n/3N$, and

$$U = 3NRTP + 3N\gamma(1 - P). \tag{1}$$

In the case of a solid the kinetic energy of a degree of freedom is on the average equal to its potential energy. We may assume, therefore, that the probability for a certain value of the potential energy is equal to the probability for the same value of the kinetic energy. By Maxwell's distribution law, the probability that the relative velocity of two atoms along the line of their centers shall lie between $|u|$ and $|u + du|$ is

$$\frac{2}{\alpha\sqrt{\pi}}e^{-\frac{u^2}{\alpha^2}}du,$$

where

$$\alpha = 2\sqrt{\frac{RT}{m}}.$$

This is therefore also the probability that the relative kinetic energy shall lie between $\frac{1}{2}mu^2$ and $\frac{1}{2}m(u + du)^2$. Since the probability for the potential energy is equal to that for the kinetic energy, the probability that the relative potential energy shall lie between $\frac{1}{2}mv^2$ and $\frac{1}{2}m(v + dv)^2$ is similarly,

$$\frac{2}{\alpha\sqrt{\pi}}e^{-\frac{v^2}{\alpha^2}}dv.$$

Thus the probability that the total energy shall lie between $\frac{1}{2}m(u^2 + v^2)$ and $\frac{1}{2}m\{u^2 + v^2 + d(u^2 + v^2)\}$ is the product of these two expressions, or

$$\frac{4}{\alpha^2\pi}e^{-\frac{u^2}{\alpha^2}}e^{-\frac{v^2}{\alpha^2}}dudv.$$

If we let ϵ be the critical value of the energy below which a degree of freedom remains agglomerated, the probability that the degree of freedom shall be agglomerated is:

$$P' = \int_0^{\frac{1}{2}m(u^2+v^2)=\epsilon} \frac{4}{\alpha^2\pi} e^{-\frac{u^2}{\alpha^2}} e^{-\frac{v^2}{\alpha^2}} du dv,$$

$$= \frac{4}{\alpha^2\pi} \int_0^{u^2=\frac{2\epsilon}{m}} e^{-\frac{u^2}{\alpha^2}} du \int_0^{v^2=\frac{2\epsilon}{m}-u^2} e^{-\frac{v^2}{\alpha^2}} dv,$$

or

$$= \frac{4}{\alpha^2\pi} \int_0^{\beta} e^{-\frac{u^2}{\alpha^2}} du \int_0^{\sqrt{\beta^2-u^2}} e^{-\frac{v^2}{\alpha^2}} dv;$$

where

$$\beta^2 = \frac{2\epsilon}{m}.$$

This integral may be determined by a series method, the solution being,

$$P' = \frac{\beta^2}{\alpha^2} - \frac{1}{2!} \frac{\beta^4}{\alpha^4} + \frac{1}{3!} \frac{\beta^6}{\alpha^6} - \cdots.$$

This is the probability that a possible degree of freedom shall be agglomerated. The probability that it shall actually exist is therefore:

$$P = 1 - P'$$

$$= 1 - \frac{\beta^2}{\alpha^2} + \frac{1}{2!} \frac{\beta^4}{\alpha^4} - \frac{1}{3!} \frac{\beta^6}{\alpha^6} + \cdots.$$

But

$$e^{-\frac{\beta^2}{\alpha^2}} = 1 - \frac{\beta^2}{\alpha^2} + \frac{1}{2!} \frac{\beta^4}{\alpha^4} - \frac{1}{3!} \frac{\beta^6}{\alpha^6} + \cdots,$$

and by comparison of series,

$$P = e^{-\frac{\beta^2}{\alpha^2}}.$$

We may substitute for β^2/α^2 its equivalent,

$$\frac{\beta^2}{\alpha^2} = \frac{\frac{2\epsilon}{m}}{\frac{4RT}{m}} = \frac{\epsilon}{2RT} = \frac{\tau}{T}, \quad \text{where} \quad \tau = \frac{\epsilon}{2R},$$

then

$$P = e^{-\frac{\tau}{T}}. \tag{2}$$

Substituting this value of P in equation (1) we have:

$$U = 3NRTe^{-\frac{\tau}{T}} + 3N\gamma(1 - e^{-\frac{\tau}{T}}), \tag{3}$$

and the specific heat is:

$$C_v = \frac{dU}{dT} = 3NRe^{-\frac{\tau}{T}} + \frac{3NR\tau}{T} e^{-\frac{\tau}{T}} - 3N\gamma \frac{\tau}{T^2} e^{-\frac{\tau}{T}}. \tag{4}$$

Since there is a T^2 in the denominator of the last term, it is evident that as long as γ has a finite value, T can be made so small that C_v will become negative. This is impossible, as it implies a condition of instability, so we must place $\gamma = 0$, and

$$C_v = 3NRe^{-\frac{\tau}{T}}\left(\frac{\tau}{T} + 1\right). \tag{5}$$

If $T = \infty$, $C_v = 3NR = C_\infty$,

$$\therefore \frac{C_v}{C_\infty} = e^{-\frac{\tau}{T}}\left(\frac{\tau}{T} + 1\right). \tag{6}$$

This is the expression for the variation of the specific heat with temperature to which our assumption leads.

TESTING THIS EQUATION.

The curves of Fig. 1 show how this formula compares with that of Debye for the specific heat.[1] The solid line is plotted from equation (6)

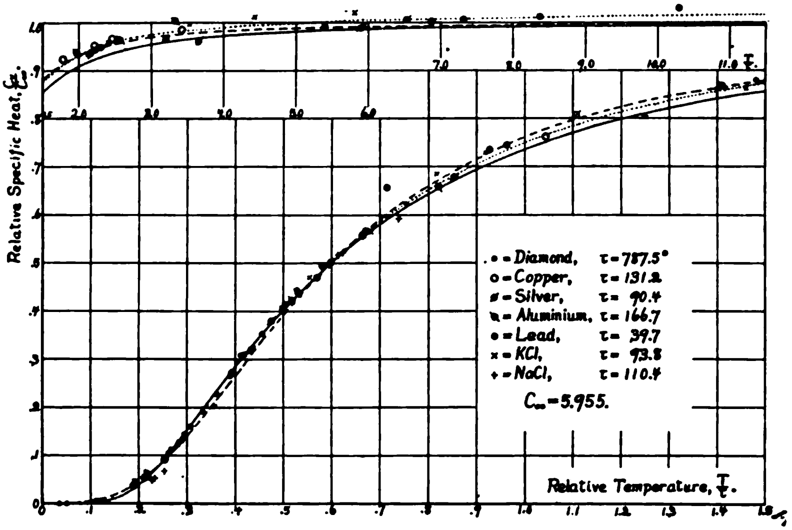

Fig. 1.

and the broken one from Debye's equation,

$$\frac{C_v}{C_\infty} = \frac{12}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{3x}{e^x - 1},$$

where $x = \Theta/T$. The two curves have been made to coincide at $C_v/C_\infty = 0.5$. That they are in general good agreement is evident at a glance.

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[1] Debye, Ann. d. Phys., 39, 789. Debye's formula is used because his has been shown to be the most accurate of any of the existing expressions (cf. E. H. Griffiths and E. Griffiths, Proc. Roy. Soc., A, 90, 558).

Their comparative accuracy has been tested with the data used by Debye and by Nernst and Lindemann[1] in testing their own formulæ. I have taken their calculations of C_v from the observed value of C_p. The value of γ for each of the substances is chosen so as to bring the experimental values as near as possible to the two curves where they cross.[2]

At lower temperatures, though the curves are not far apart, there is an evident preponderance of experimental evidence in favor of the solid curve. Above $T/\tau = 0.6$, however, the experimental values gradually rise from the solid curve, cross the broken one at about 2.25, and continue approximately parallel to the solid curve but at a higher level. The dotted curve is drawn as an approximate experimental mean. It is evident that the data fit neither formula accurately for these temperatures, but that the values of C_v/C_∞ approach a limit some two per cent. higher than unity. That these high values of C_v are not due to proximity to the melting point is evident when one notices that none of the experiments are made at a temperature closer than 191° to the melting point, while in the case of KCl the value of C_v/C_∞ rises above unity when the temperature is only .40 as high as the melting point. A possible explanation of the high values of the specific heat at these temperatures is that there may be more degrees of freedom in a solid than indicated by Rayleigh's formula, $C_\infty = 3R$. Whatever the cause of this discrepancy, however, it is necessary on any theory that C_v shall never become greater than C_∞, so we must assume a value of C_∞ greater than $3R = 5.955$, which is the value used in calculating the values of C_v/C_∞ in Fig. 1. The value 6.081 has therefore been chosen as an experimental limit which C_v seems to approach.

Fig. 2 shows the same theoretical curves and the experimental data plotted with this new value of C_∞. The curves have here been made to coincide at $C_v/C_\infty = 0.65$, in order to show more clearly the differences between the two formulæ. It will be seen that this correction makes the observed specific heats conform very well with the curve plotted according to my expression, while they vary consistently from that of Debye. Thus while the data can in no way be made to conform at all temperatures with Debye's formula, by making a correction which would seem necessary in any case, the data may be made to fit well the equation

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[1] Zeitschr. für Electrochemie, 17, p. 817.

[2] In the following tables the values of C_v for Al, Pb, KCl and NaCl are taken from Nernst and Lindemann's paper (*loc. cit.*), those for Cu, Ag and diamond from that of Debye (*loc. cit.*). C_v is calculated from the observed values of C_p according to the formula, due to Nernst and Lindemann, $C_v = C_p - 0.0214 C_p^2 T/T_s$, where T_s is the melting point of the substance. C_∞ is taken to be 6.081 as explained in the text.

T	C_v Obs.	C_v Calc.
Diamond, τ = 794.0°		
30°	0.00	0.00
42	0.00	0.00
88	0.03	0.01
92	0.03	0.015
205	0.62	0.63
209	0.66	0.67
220	0.72	0.75
222	0.76	0.80
232	0.86	0.87
243	0.95	0.98
262	1.14	1.18
284	1.35	1.41
306	1.58	1.60
331	1.83	1.87
358	2.11	2.13
413	2.64	2.62
1169	5.24	5.18
Copper, τ = 133.5°		
23.5°	0.22	0.14
27.7	0.32	0.26
33.4	0.54	0.56
87	3.32	3.32
88	3.37	3.36
137	4.53	4.54
234	5.50	5.40
290	5.66	5.60
323	5.75	5.69
450	5.87	5.86
Lead, τ = 38.4°		
23.0°	2.95	3.04
28.3	3.91	3.69
36.8	4.38	4.38
38.1	4.43	4.45
85.5	5.57	5.60
90.2	5.63	5.67
200	5.91	5.98
273	5.99	6.02
290	5.99	6.02
332	6.03	6.03
409	6.15	6.05
Silver, τ = 92.0°		
35.0°	1.58	1.58
39.1	1.90	1.93
42.9	2.26	2.25
Silver (continued)		
45.5°	2.46	2.44
51.4	2.80	2.83
53.8	2.89	2.98
77.0	4.04	4.04
100	4.80	4.65
200	5.61	5.61
273	5.75	5.79
331	5.71	5.87
535	5.90	5.93
589	5.99	5.99
Aluminum, τ = 169.6°		
32.4°	0.25	0.19
35.1	0.33	0.28
83.0	2.40	2.40
86.0	2.51	2.51
88.3	2.61	2.60
137	3.91	3.94
235	5.17	5.09
331	5.58	5.55
433	5.74	5.72
555	5.98	5.85
NaCl, τ = 113.5°		
25.0°	0.29	0.36
25.5	0.31	0.38
28.0	0.40	0.52
67.5	3.05	3.04
69.0	3.12	3.10
81.4	3.52	3.60
83.4	3.72	3.71
138	4.79	4.87
235	5.55	5.57
KCl, τ = 96.1°		
26.9°	0.76	0.78
33.7	1.25	1.35
39.0	1.83	1.80
52.8	2.79	2.78
63.2	3.34	3.34
76.6	4.08	3.91
86.0	4.33	4.22
137	5.18	5.15
235	5.73	5.69
331	5.93	5.87
416	6.02	5.95
550	6.09	5.99

just derived. In fact, all variations from the theoretical values seem to lie within the limits of experimental error.

Discussion of the Formula.

Some interesting aspects of formula (6) appear if the exponent of e is written in a different form. τ is defined as $\epsilon/2R$, where ϵ is the energy required to liberate an agglomerated degree of freedom. This quantity has the same dimensions as Planck's energy quantum $h\nu$, both being elementary units of energy. In fact Benedicks has shown,[1] from a consideration of the relation of hardness to the frequency of vibration of an atom, that ϵ is probably proportional to ν. If we call the factor of proportionality b, the probability becomes

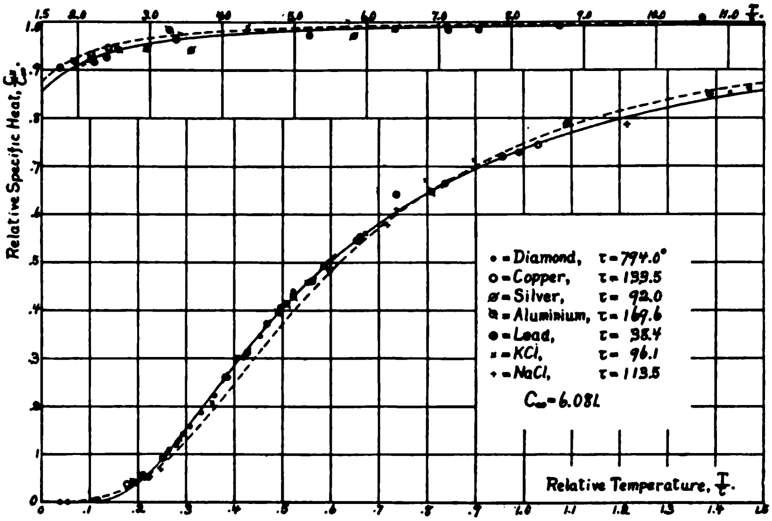

Fig. 2.

$$P = e^{-\frac{\tau}{T}} = e^{-\frac{\epsilon}{2RT}} = e^{-\frac{b\nu}{2RT}} = e^{-\frac{\beta\nu}{T}}, \tag{7}$$

where

$$\beta = \frac{b}{2R}.$$

The value of β can easily be determined from the expression $\beta = \tau/\nu$, which follows from equation (7). The values of τ for the different substances considered are determined by their specific heats as shown in Fig. 2. The values of ν may be taken as those assigned by Nernst and Lindemann's formula for the specific heat, since their values of ν have been shown to be in very accurate agreement with the characteristic frequencies of those substances whose reststrahlen can be obtained. The different values of β as thus determined are given in the following table.

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[1] *Loc. cit.*

Substance.	τ	$\nu \times 10^{-12}$	$\beta \times 10^{11}$	Difference from Mean.
Lead	38.4	1.9	2.02	+0.3%
Silver	92.0	4.5	2.04	+1.4
KCl	96.1	4.73	2.03	+0.6
NaCl	113.1	5.8	1.96	−2.9
Copper	133.5	6.6	2.02	+0.3
Aluminium	169.6	8.3	2.04	+1.4
Diamond	794.0	40.0	1.98	−1.4

β is thus determined just as accurately as ν is known, and since it remains constant over so great a range of frequencies, equation (7) may be considered valid, even though its derivation is not rigid.

It is interesting to see how the quantity b in this equation compares with the similar quantity h of Planck's expression. b is determined by the equation $b = 2R\beta$, in which the accepted value of R is about 1.35×10^{-16} erg deg.$^{-1}$, and $\beta = 2.01 \times 10^{-11}$ deg. sec. Thus

$$b = 5.44 \times 10^{-27} \text{ erg sec.},$$

while Planck's constant h has the value

$$h = 6.55 \times 10^{-27} \text{ erg sec.}$$

The value for b found here is in excellent agreement with certain values of h as determined by photoelectric methods: Richardson and Compton[1] 5.4×10^{-27}; Hughes[2] 5.6×10^{-27}; Cornelius[3] 5.7×10^{-27}; though Kadesch[4] and Millikan[5] very recently have obtained photoelectric values of h more nearly 6.55×10^{-27}.

Now that equation (7) has been established we are in a position to make a new application of Debye's theory which interprets the heat energy of solids in terms of their elastic vibrations. He considers a whole spectrum of frequencies, the number of vibrations between the frequencies ν and $\nu + d\nu$ being

$$dn = \frac{9N}{\nu_m^3}\nu^2 d\nu, \tag{8}$$

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[1] Phil. Mag., 24, 574.

[2] Phil. Trans. Roy. Soc., 212, 205.

[3] K. T. Compton, PHYS. REV., 1, 382.

[4] PHYS. REV., 3, 367.

[5] PHYS. REV., 4, 73.

where $3N$ is the total number of degrees of freedom in the solid, and ν_m is the maximum possible frequency, determined by the equation:

$$\frac{1}{\nu_m{}^3} = \frac{4\pi V}{9N}\left\{2\left(\frac{2\rho(1+\sigma)\chi}{3(1-2\sigma)}\right)^{\frac{3}{2}} + \left(\frac{2\rho(1+\sigma)\chi}{3(1-\sigma)}\right)^{\frac{3}{2}}\right\}, \tag{9}$$

where V is the volume, ρ the density, χ the compressibility, and σ Poisson's ratio, for the substance considered. The average energy of a degree of freedom of frequency ν is, by equations (3) and (7),

$$\frac{3NRTe^{-\frac{\beta\nu}{T}}}{3N} = RTe^{-\frac{\beta\nu}{T}}; \tag{10}$$

so the total energy in the solid is

$$U = \int_0^{\nu_m}\frac{9N}{\nu_m{}^3}\nu^2 \cdot RTe^{-\frac{\beta\nu}{T}},$$

$$= \frac{9NRT}{\nu_m{}^3}\left\{\frac{2T^3}{\beta^3} - e^{-\frac{\beta\nu_m}{T}}\left(\frac{T}{\beta}\nu_m{}^2 + \frac{2T^2}{\beta^2}\nu_m + \frac{2T^3}{\beta^3}\right)\right\}.$$

Substituting $\tau = \beta\nu_m$,

$$U = 9NRT\left\{\frac{2T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(\frac{T}{\tau} + \frac{2T^2}{\tau^2} + \frac{2T^3}{\tau^3}\right)\right\}.$$

According to Debye's assumptions ν_m, and hence also τ, are not functions of T, so the specific heat is:

$$C_v = \frac{dU}{dT} = 9RN\left\{8\frac{T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(8\frac{T^3}{\tau^3} + 8\frac{T^2}{\tau^2} + 4\frac{T}{\tau} + 1\right)\right\},$$

and

$$\frac{C_v}{C_\infty} = 3\left\{8\frac{T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(8\frac{T^3}{\tau^3} + 8\frac{T^2}{\tau^2} + 4\frac{T}{\tau} + 1\right)\right\}. \tag{11}$$

Fig. 3 shows how this expression compares with equation (6). The solid line as before represents the first equation derived, while the broken one represents equation (11). Although the difference between these two curves is not large, it is evident, particularly at low temperatures, that this new formula does not represent the facts accurately. It is necessary to conclude, therefore, either that the energy of each degree of freedom is not accurately expressed by equation (10) or that some of the assumptions on which Debye's theory is based are not valid.

It is evident that if equation (11) is to be valid, ν_m must not vary with the temperature. That is, by equation (9), the quantities σ and χ must be independent of the temperature. While there is no evidence of any considerable variation in the value of σ, Grüneisen has shown[1]

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[1] Ann. d. Phys., 33, 1239. Some of Grüneisen's results indicating such a variation of the compressibility with the temperature may be given:

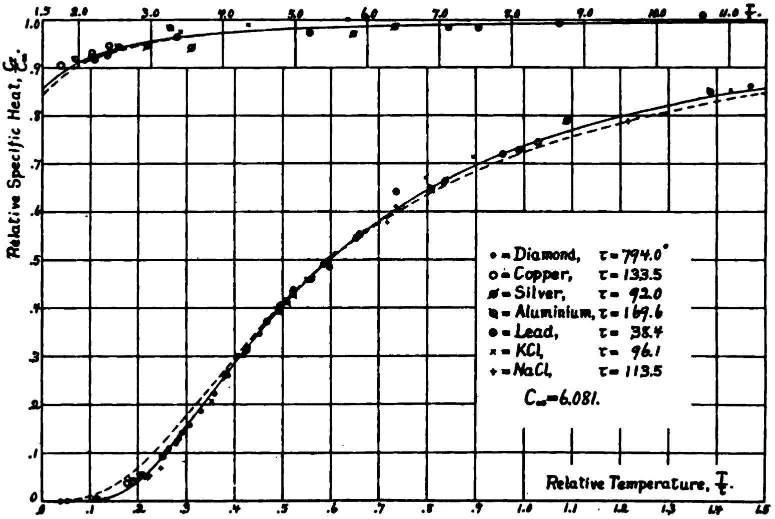

Fig. 3.

Compressibility $\times 10_6$.

T	Al	Fe	Cu	Ag	Pt	Sn	Pb
83°	1.32	0.606	0.718	0.709	0.374	2.1	2.5
290	1.46	0.633	0.773	0.763	0.392	3.1	3.2
373	1.70	0.652	0.801	0.820	0.398	—	—

that there is a general and decided increase in the compressibility χ with the temperature. It is evident, therefore, that account must be taken of the variation of ν_m with the temperature. If this is done, equation (11) becomes:

$$\frac{C_v}{C_\infty} = 3\left\{8\frac{T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(8\frac{T^3}{\tau^3} + 8\frac{T^2}{\tau^2} + 4\frac{T}{\tau} + 1\right)\right.$$
$$\left. - \left[6\frac{T^4}{\tau^4} - e^{-\frac{\tau}{T}}\left(6\frac{T^4}{\tau^4} + 6\frac{T^3}{\tau^3} + 3\frac{T^2}{\tau^2} + \frac{T}{\tau}\right)\right]\frac{d\tau}{dT}\right\}.$$

The order of magnitude of $d\tau/dT$ is 5×10^{-4}, so the last term is negligible except at high temperatures; but instead of considering τ to be constant, its particular value which corresponds to the temperature for which C_v/C_∞ is evaluated must be employed in order to make equation (11) valid. In the case of aluminum, for example, the compressibility at 373° is 29 per cent. greater than at 83°. This corresponds to a difference in ν_m, and hence also in τ of 13.5 per cent., and in the specific heat at the lower temperature of about 45 per cent. Thus if the specific heat of aluminum at 83° is calculated from its elastic constants at 373°

the resulting value is some 45 per cent. greater than if calculated from its constants at the lower temperature. This shows conclusively that equation (11) is not valid if τ is considered independent of the temperature.

That the same argument applies to Debye's formula for the specific heat is shown by the form of his equation at low temperatures,

$$\frac{C_v}{C_\infty} = 77.93\frac{R^3T^3}{h^3\nu_m{}^3}.$$

In this equation the value of the ratio C_v/C_∞ for aluminum varies 46 per cent. according as the value of ν_m is calculated from the elastic constants at 373° or at 83°. It is thus evident that the error introduced by Debye's assumption that ν_m is independent of the temperature is much too large to be neglected.

It can be shown, moreover, that the fundamental assumption on which Debye's theory is based, that the heat energy of a solid lies in the elastic vibrations of the body as a whole, does not represent the truth. It may be shown that the velocity of propagation of a thermal disturbance in a solid is directly proportional to the diameter of the elementary vibrator. If, as Debye assumes, the whole substance is capable of vibrating as a unit in its heat motion, the thermal conductivity should therefore be very great. This may be shown more clearly in the following manner. Consider two infinite parallel planes in an elastic medium, at one of which the medium is maintained with vibrational energy greater than at the other corresponding to a difference in temperature of one degree. The thermal conductivity, or rate at which energy is transmitted from the hotter to the colder plane per unit area will then be equal to the product of the difference in the energy content of the medium at the two planes by the velocity of transmission of the vibrational disturbance; *i. e.*:

$$\text{thermal conductivity} = V \cdot C(t_1 - t_2) = V \cdot C,$$

where C is the heat capacity per unit volume of the medium, and V is the mean velocity of propagation of a vibrational disturbance. For aluminum C is about 0.5 calories cm.$^{-3}$ deg.$^{-1}$, and V may be taken as about 5×10^6 cm. sec.$^{-1}$, so the thermal conductivity should be of the order of magnitude of 2.5×10^5 calories cm.$^{-2}$ sec.$^{-1}$ deg.$^{-1}$. This is wholly out of accord with the experimental value, which is 0.5 calories cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$. In fact the dimensions themselves are different, the rate of heat transmission according to this assumption being independent of the distance apart of the two parallel planes. It is evident, therefore, that the heat energy of solids is not contained in the elastic vibrations of the body as a whole, but is contained in the motion of very much smaller elements. Since the lower limit of the frequencies which enter into Debye's theory is determined by the dimensions of the vibrator, the range of frequencies in which thermal motion occurs is thus limited. If the elementary vibrator is of atomic dimensions, the only frequencies to be considered are the natural frequencies of the atoms themselves.[1] Thus the assumption that thermal motion occurs in all the possible frequencies from o to ν_m cannot be accepted.

Debye's formula for the specific heat must therefore be considered to be largely empirical. In order to compare the results of this agglomeration hypothesis with those of the quantum hypothesis, equation (6) should be compared rather with Einstein's formula,[2]

$$\frac{C_v}{C_\infty} = \frac{h^2\nu^2}{R^2T^2}\frac{e^{h\nu/RT}}{(e^{h\nu/RT} - 1)^2},$$

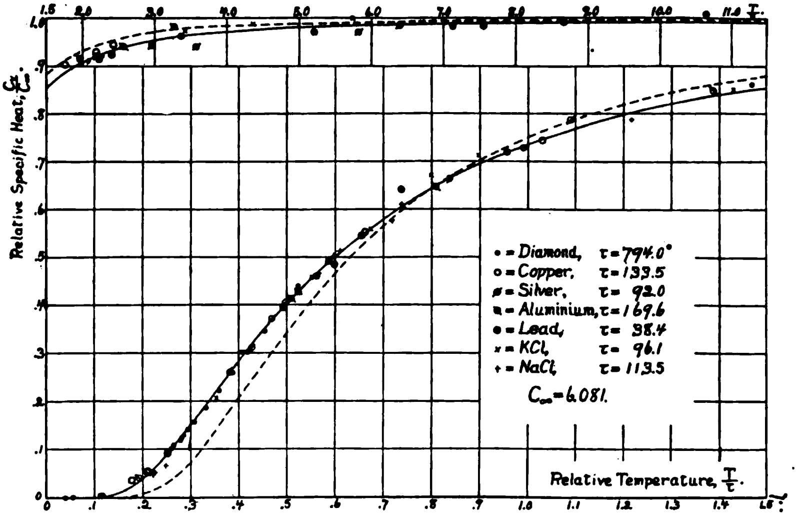

Fig. 4.

which is a valid deduction from the quantum hypothesis. Fig. 4 shows how these two expressions compare. The solid line represents my formula and the broken one that of Einstein. The experimental values are the same as in Fig. 2. It is evident that Einstein's expression is much the less accurate of the two. Thus from the standpoint of the variation of specific heat with temperature the assumption is strongly supported that at sufficiently low temperatures many of the atoms of a solid become so intimately associated that they lose degrees of freedom.

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[1] The great increase in thermal conductivity at low temperatures may be shown to indicate that the diameter of the elementary vibrator becomes comparatively large at low temperatures. Under these circumstances Debye's assumption of a whole spectrum of frequencies may be valid. This may account for the fact that at extremely low temperatures, $T/\tau = 0$ to 0.22, the observed specific heats are slightly larger than indicated by equation (6). If this be true, equation (11) should hold at these temperatures, and Debye's "third power law" would still be true.

[2] Einstein, Ann. d. Phys., 22, 180.

Summary.

The assumption has been made that a possible degree of freedom between two atoms in a solid actually exists only as long as the relative energy between the two atoms is greater than a certain critical value.

An expression for the variation of the specific heat of solids with temperature has been derived from this assumption, which seems to agree more satisfactorily with experiment than any of the existing formulæ.

Debye's expression for the variation of the specific heat with temperature has been found to be largely empirical; so to compare this agglomeration hypothesis with the quantum hypothesis my formula is rather to be compared with that of Einstein.

The strong support of experimental evidence in this case seems to indicate that this agglomeration hypothesis represents more accurately the condition of the atoms in a solid than does the quantum hypothesis.

I wish to express my thanks to Professor Adams and Professor Magie for their continued interest in this study.

Palmer Physical Laboratory,
Princeton, N. J.,
May 5, 1915.

A HIGHLY SENSITIVE ELECTROMETER.

By A. L. Parson.

FOR the measurement, and more particularly the detection, of very small potential differences on open circuit a very highly sensitive electrometer was required. The most sensitive hitherto described is the "duant" electrometer of Hofmann[1] which has a capacity of only 5 cm. and may be adjusted to work in a condition approaching instability. It can then give deflections at the rate of 10 mm. per millivolt (scale distance 1.5 meters), but he does not state whether it is steady enough in its action to detect a single 10^{-4} volt unit by a 1 mm. deflection, the only results given from which the steadiness can be judged being for the lower sensitivity of 1 *mm/mv.* This instrument suffers from the disadvantage of requiring a needle of extremely delicate and exact construction, but a more troublesome feature is the complexity of the electrical system used in its operation. The suspension is made conducting and the potential to be measured is communicated to the needle, while the two conductors which take the place of quadrants must be kept at a high potential difference by a constant battery: it is by a careful adjustment of this potential difference that the maximum sensitivity is obtained.

The principle of working with a condition approaching instability has also been used greatly to increase the sensitivity of the gold-leaf electroscope by C. T. R. Wilson, and of the string electrometer by Wulf, but neither of these has the inherent sensitivity of the suspended needle electrometer, of which the most familiar form is of course that of Dolezalek. This instrument, in its ordinary form, can give, with very fine quartz fibers, deflections at the rate of 10 mm. per millivolt, but is then somewhat uncertain and slow in its action. Its capacity is about 50 cm. and probably could not be made less without diminishing its sensitivity to potential differences. The necessity of securing a uniform inducting surface inside the quadrants also makes against a small capacity, for the gaps must be small and the quadrant edges thick.

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[1] Ann. d. Phys. [4], 42, pp. 1196–1220, 1913.

The Principle of the Instrument.

The instrument about to be described is a modification of the quadrant electrometer, which does not suffer from these disadvantages, and which by an ability to work in a condition approaching instability can be made very much more sensitive. To a certain extent, however, it loses the good feature of giving a deflection proportional to the potential difference.

The four quadrants are replaced by four sectors arranged in pairs AB, $A'B'$, as in Fig. 1, and the box form of the quadrants is abandoned, the sectors being cut from a single disc of metal .5 mm. thick. In the quadrant electrometer the torsion of the quartz fiber is used as a measure of the force on the needle, and is the only source of its stability: in the present case, however, the stability of the needle is procured by an automatic disposition of electric forces; and the torsion of the fiber is useful only for balancing any disymmetry in the electric forces such as may arise from a slightly uneven mounting of the sectors. In the more sensitive adjustments of the instrument, however, this control by the torsion head is very valuable.

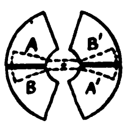

Fig. 1.

As regards the electrical connections, the instrument can be used in exactly the same way as the quadrant electrometer, and the needle can be charged either by a constant battery through a conducting suspension, or by the simpler method of a charging switch.

The chief innovation is that the sectors are mounted on a pair of arms pivoted scissors-like at the center, and that the small gaps between A and B, A' and B' can be varied in width from something very small to about 2 mm. by the action of a micrometer screw. When the gap is small and the sectors are at equal potentials, A and B form a virtually continuous inducing surface opposite the charged needle and the capacity of the system is highest when the needle hangs symmetrically over them: this therefore is its stable position. If a difference of potential is set up between AA' and BB', the needle is deflected, at first nearly proportionally to the potential difference, and then less and less as it approaches the large gaps at the sides. This is the least sensitive way of using the instrument, and gives deflections at the rate of about 3 mm. per millivolt (the scale being 5 meters distant[1]). As the gap between A and B is widened, the needle becomes less and less stable in its central position and the sensitivity greater and greater. Just before instability is reached a stable deflection at the rate of as much as 150 mm. per millivolt can be obtained, but it is probably not worth while working with deflections greater than about 40 mm. per millivolt, as will appear later.

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[1] It was found possible to use this great scale distance profitably by placing the telescope near the instrument and at an angle. If the plane of incidence of the light on the mirror is horizontal, the scale divisions are blurred owing to reflection at both the surfaces of the mirror glass; but if the plane is vertical, as when the scale is placed high up and the telescope is inclined upwards towards the mirror, this does not occur. The increased sensitivity due to the use of this greater scale distance is valuable in itself, but is not of course a property of

It is of interest to notice that when the sectors are very close, and the instrument least sensitive, the sensitivity increases as the potential to which the needle is charged diminishes. This might have been predicted, for, while the deflecting force is proportional to the first power of the charge on the needle, the electrical force giving it stability is more nearly proportional to the square of it. Some values got with an older model, in which the needle was 3 cm. long and the quartz fiber thin enough for its torsion to be almost negligible, are as follows:

Potential of needle in volts	80	40	20	10
Deflection in mm. per millivolt	2.1	3.8	5.3	9

But there is no advantage in using the lower potentials, for the maximum sensitivity attainable is not at all increased, while the period of deflection is greatly lengthened. All the results given in this paper were got with a needle potential of + 80 volts. (The fact that a positive charge is lost to the air less rapidly than a negative one was pointed out in connection with electrometers by Lord Kelvin: the difference cannot be great at 80 volts, however.)

One of the chief advantages of this instrument is that its sensitivity to potential differences is quite independent of the scale on which it is built, for the torsion of the suspension is not a determining factor unless it is altogether too thick. As it is easy to get a quartz fiber .002 mm. thick, which would suit a needle .5 cm. long, it is evident that the capacity can be made very small. Actually, the limiting factor is the smallest mirror with which a scale can be read at a distance of say 1 meter. This is about 2 mm. square and would have too great a moment of inertia for a needle less than about .7 cm. long. In a trial instrument the needle was 3 cm. long, but in the one now to be described it is 1.8 cm., and the disc from which the sectors were cut was 2.1 cm. in diameter, with a .75 cm. hole in its center. The capacity was found to be 9 cm. by a method of induction through a condenser of known and variable capacity.

Constructional Details (Fig. 2).

The most convenient arrangement of parts was found to be given by making a base *A* (carrying the sectors and provided with suitable widely-

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the electrometer. To compare with Hofmann's result of 10 mm. per millivolt, for example, which was got at a scale distance of 1.5 meters, the sensitivity values here given should be divided by 3.3. Hofmann used a spot of light instead of a reading telescope and read the scale to .5 mm. only.

spread feet) to which the rest of the instrument (all in one piece) was attached by a spring fit of its cylindrical case *B* around a flange at *C*. The case, which is only 5 cm. in diameter and 4.5 cm. high, is made small in order to diminish the effect of air currents within it, even though the electrical capacity may thus be raised by a unit or so.

The micrometer screw and terminal could be made to come up from below; but this would be inconvenient on so small a scale, and hence they are fixed in curved pads *D* (of brass and vulcanite respectively) which are attached to the base and rest tightly over slots *E* in the cylindrical case when this is pressed down into position. A good fit here is essential in order to avoid disturbance from air-currents.

For the window, which is 1.5 cm. square, a microscope cover slip was found to be optically satisfactory, although a piece of a slide was not. As the window opening is a possible source of electrical disturbance, it is provided with a divergent metal shade *S* projecting 2 cm. This has the further advantage of partly protecting the interior from light: it was noticed that the light (or heat) from a 40-watt lamp at a meter's distance, suddenly falling on the interior, gave rise to a very marked disturbance.

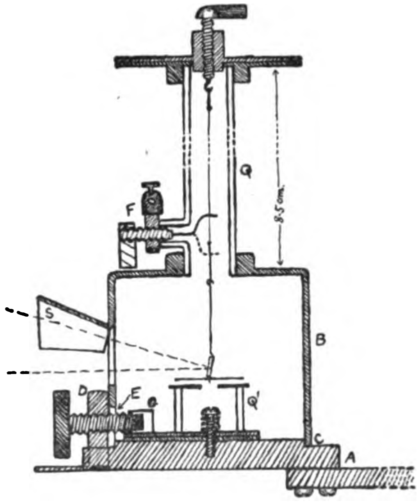

Fig. 2.

The torsion head, which is of any suitable construction, is supported on a quartz tube *Q* fixed to the top of the case. The use of quartz here serves the double purpose of insulating the torsion head (if this should ever be required) and of reducing to a minimum the effect of temperature changes on the distance between the needle and the sectors. This effect would be expected to give more trouble in the present instrument than in one where the needle hung midway between the upper and lower surfaces of quadrants, but it is not yet certain that the precaution is necessary in practice. Since in the ordinary use of the instrument, the exact potential of the needle is not important, provided it remains constant, the needle is charged by means of a switch *F*, which comes through a side tube on the quartz column, and by a rotary motion brings a platinum wire into contact with the lower hook (also of platinum) of the suspension. A light metal shield slipped over the lower part of the quartz tube gives electrical protection at this point.

As regards the insulation, the use of sulphur is difficult on so small a scale, but if the interior is kept dry, clean quartz serves the purpose very well (with phosphorus pentoxide in the case, which it should be said was shown in this way to be by no means impervious to moist air, charge was lost at the rate of about 1 per cent. per minute).[1] Two of the sectors are therefore mounted by means of sealing wax on small quartz rods Q' set on one of the scissors arms, and are connected to the terminal by a fine wire which is previously soldered to them and enters the case through a narrow quartz tube. The other two are soldered to short lengths of wire, and not insulated. Quite the most troublesome part of the whole construction was the setting of the four sectors accurately in one plane parallel to the base, and at the right distances apart.

The micrometer screw may operate by a cone and jaws arrangement but in the present case the end of the screw is squared off and works between glass plates G set at an angle on the arms carrying the sectors.

The needle can be made from a single thickness of thin paper rubbed with graphite on both sides, but the use of the drying agent is then liable to alter its shape; so recourse is had to aluminium. It is made very light by using very thin foil and then by thinning the two ends by dipping in hydrochloric acid until they begin to show signs of disintegration. In this way the weight has been reduced to 3 mgm. The weight of the mirror (10 mgm.) is less important on account of its smaller moment of inertia, while that of the platinum stem (17 mgm.) is of course relatively unimportant. As the needle was fixed to its stem by a little sealing wax, it was found essential to secure electrical contact here by a drop of starch paste (covered with paraffin wax to protect it from the drying agent). To obviate any angular play at the hook connections in the suspension, the usual device of making one of each pair of hooks out of the *flattened* end of a fine wire was adopted.

The present instrument requires a quartz fiber .006 mm. thick and 6 cm. long: this could be made thinner and only 1 cm. long or even less with advantage, for the disturbing effect of vibrations would then be lessened. The mirror is 4 mm. by 3.5 mm., and was cut from a thin galvanometer mirror.

THE SHAPE OF THE SECTORS AND NEEDLE.

It will be evident from an inspection of Fig. 1 that the smaller the angle subtended by the sectors, the less will be the sensitivity. At the same time the large gaps at the sides should not be too much encroached upon, or the needle will hardly be stable in its central position even when the small gaps are made as small as possible. It is found that sectors subtending 70° each give good results.

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[1] Most of this must be due to the projecting part of the terminal, which is not kept dry.

The shape of the needle is a matter of the greatest importance. The effect of its width and curvature, and of its distance from the sectors, upon what might be called the "angular capacity gradient" of the system for different widths of the sector gap is somewhat complex, and required a good deal of study for its elucidation. It was found that the needle can in general be stable either in the symmetrical position, or in an unsymmetrical position well to one side, and in either case the sensitivity can be adequately controlled by altering the width of the sector gap. But in the case of the unsymmetrical position the suspension must have a permanent twist, and this gives a troublesome "drift" of the needle due to its slow loss of charge; so that attempts to use this were abandoned.

In Fig. 3 are shown curves for the behavior of the needle in its symmetrical stable position (the quartz fiber used being .004 mm. thick): the first number written over each curve gives the width of the needle in millimeters, and the second its distance from the sectors. It may be seen that the sensitivity increases as the needle becomes narrower and as it is brought closer to the sectors. The best needle is obviously

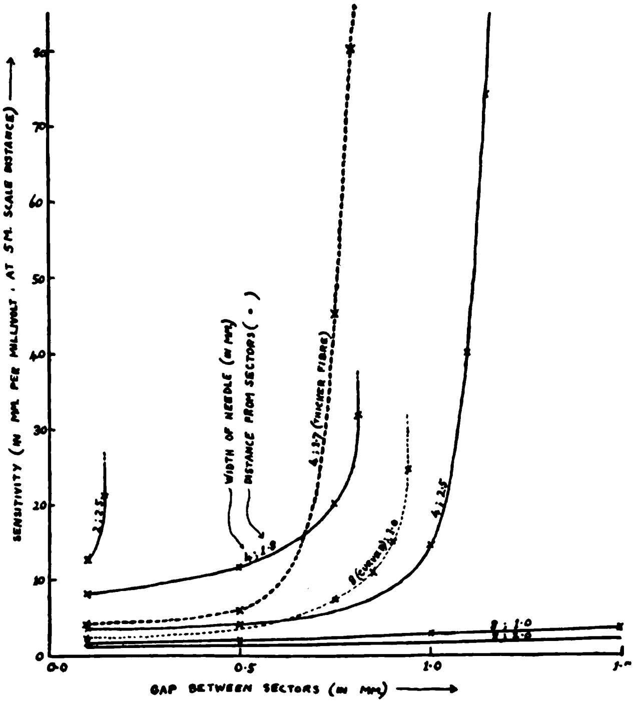

Fig. 3.

flat and about 4 mm. wide: the ratio of the width to length is thus about 1 : 4, and this would no doubt be best for an instrument of any size. It is not so easy to decide upon the best distance from the sectors. With any given suspension, the sensitivity increases as the needle comes closer, and also the period of swing is diminished, but instability arrives more suddenly as the sector gap widens. As, however, the use of a thicker fiber conduces to stability, the best result is obtained by using a relatively thick fiber (.006 mm.) and lessening the distance from the sectors. This plan, which combines the shorter period of swing got at the smaller distance with the flexibility got at the greater, gives the curve shown by the thick dotted line in the figure. (The thin dotted line is for a needle somewhat convex on its lower side.)

THE USE OF THE INSTRUMENT.

The torsion head is turned until the needle seems to hang symmetrically, and the latter is then charged. Now the telescope is placed at some convenient position near the window so that the scale can be seen, and the instrument roughly calibrated at this adjustment by a potentiometer. It will usually be found that the region of greatest sensitivity is not exactly at the point of zero potential, so the torsion head is turned until this state is secured, and the telescope moved again if necessary. On increasing the sensitivity by widening the sector gap, the region of greatest sensitivity remains nearly still, and any slight deviation may be corrected by repeating the above process.

Even with the symmetrical adjustment of the system there was often a slight "drift" of the needle, but the use of phosphorus pentoxide inside the case made this practically to disappear. The nature of the remaining drift and of other disturbances that occur will be seen from the following typical results. Runs over the whole scale are given at sensitivities of about 7 and about 40 mm. per millivolt, and also deflections obtained for separate 10^{-2}, 10^{-3} and 10^{-4} volt units.

It will be seen that, whereas the instrument could detect 10^{-6} volt (at a 150 *mm/mv* sensitivity) if it were steady enough, it cannot in practice detect less than about 3×10^{-5} volt, and, with the very efficient optical system used, it does this as well at a sensitivity as low as 7 *mm/mv* as at a higher. If the scale were only 1.5 meters distant, however, it would be best to use a sensitivity corresponding to about 30 *mm/mv* at the 5 meters' distance.

The cause of the unsteadiness is found to lie in an incomplete electrical shielding of the instrument; for, if the sectors are all connected to the case which is then insulated, and the whole is charged to 80 volts, a deflection corresponding to one or two millivolts is obtained. Thus

P. D. in Volts.	Scale Reading in mm.	mm./mv.
.00	573.0	
.05	886.0	
.04	831.0	5.70
.03	772.5	5.85
.02	710.5	6.20
.01	645.0	6.55
.00	575.5	6.95
−.01	505.0	7.05
−.02	439.0	6.80
−.03	378.0	6.10
−.04	320.5	5.75
−.05	266.0	5.45
.00	574.5	

Needle comes to rest in 30 sec.

Detecting 10^{-2} volt.

.00	.01	Δ
577.5	642.0	64.5
578.0	642.6	64.0
577.5	642.0	64.5
578.5	642.0	63.5
579.0	642.5	63.5

Detecting 10^{-3} volt.

.000	.001	Δ
579.5	586.0	6.5
580.0	586.5	6.5
580.0	587.0	7.0
580.0	586.5	6.5

Detecting 10^{-4} volt.

.0010	.0011	Δ
588.2	588.8	between
588.1	588.8	the
588.5	589.3	averages
588.9		+.6

.0010	.0009	Δ
588.9	588.0	between
588.7	588.2	the
588.8	588.3	averages
588.7		−.6
588.8	588.2	

P. D. in Volts.	Scale Reading in mm.	mm./mv.
.000	535	
.010	196	
.008	254	27
.006	319	32
.004	385	34
.002	455	35
.000	538	41
−.002	631	46
−.004	713	41
−.006	785	37
−.008	849	32
−.010	908	29
.000	558*	

Needle comes to rest in 90 sec.

Detecting 10^{-2} volt. (90 sec.)

.00	.01	Δ
558	900	342
558	891	333
556	897	341
565*	895	330
564	894	330
581*	910	331

Detecting 10^{-3} volt. (60 sec.)

.000	.001	Δ
592	630	38
594	632	38
590	625	35
588	623	35
596*	628	32
588	626	38

Detecting 10^{-4} volt. (40 sec.)

.0010	.0011	Δ
633	636	
632	636	between
633	638	averages
638*	639	
636.5	638.5	2.75

fluctuations of only a few volts in the "earth" charge would amply account for the disturbances observed: these fluctuations are inevitable in the neighborhood of electric lighting circuits. The defective shielding is probably due to the presence of the window, since a very good shielding of every other part of the instrument does not remove it. This difficulty will be investigated further.

The instrument becomes dead-beat when the sensitivity is raised to 15 mm. per millivolt. Its period at the higher sensitivities is not nearly as great as the time given for a reading in the table (*e. g.*, 90 sec., 60 sec., etc.), for fully two-thirds of this time is occupied by the final slow "creep" of the quartz suspension. For less accurate work good readings could be got in 20–30 sec., especially since chance disturbances would then be relatively less frequent. Also at the lower sensitivities, the first swing takes only 5 of the 30 sec. required for the needle to come to rest.

THE USE OF A FLOATING NEEDLE.

Since the torsion of the suspension is not an essential factor in its operation and stability is secured electrically, it is possible to use a floating needle. This would have the advantages of making the instrument dead-beat at all times and of eliminating the final "creep" which occupies about two-thirds of the time taken for a deflection at the higher sensitivities; but the viscous resistance of the liquid makes the instrument slow in action for needles less than 5 cm. long,[1] and also the advantage of control by the quartz fiber is lost. For the last it would be necessary to substitute an up and down adjustment of one of the sectors or something equivalent. A roughly made trial instrument with no sort of adjusting mechanism, and in which the needle takes up an unsymmetrical and very insensitive position, gives steady deflections at a sensitivity of 1 mm. per millivolt. The needle is in electrical contact with the float tank, which is insulated and kept at 80 volts, and the sectors are above instead of below the needle. The float is made of a small piece of quill tubing, and is kept vertical by a weight about 5 cm. below it. The needle is kept in its central position by the attraction of a cylindrical magnet for a little piece of iron placed on the top of the floating system.

SUMMARY.

An electrometer has been designed which can be constructed to have a capacity as low as 4 or 5 cm.,[2] and in the present model has a capacity of 9 cm. It is of simple construction and operation. Its sensitivity is great enough for the detection of 10^{-6} volt, but it has not been made steady enough as yet to detect an isolated potential difference less than about 3×10^{-5} volt in practice. It is a modification of the Dolezalek electrometer which can, by means of a mechanical adjustment, be made to work in a condition approaching instability. The way in which the stability of the needle is secured makes it possible to place it on a torsionless suspension or a float, but this plan has certain drawbacks.

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[1] That is, with the most efficient float yet constructed.

[2] Besides this, the capacity could be halved again by omitting one end of the needle and the pair of sectors below it.

THE INFLUENCE OF THE METALLIC ION IN ELECTROLYTIC SOLUTIONS UPON THE POTENTIAL DIFFERENCES BETWEEN THE SOLUTIONS AND A METALLIC ELECTRODE.

By Florella K. Finney.

The purpose of the investigation has been to determine the influence of the metallic ion in electrolytes in water solution upon the potential difference between the solution and electrodes of various metals. The method used has been to make cells containing two equimolecular solutions having different metallic ions and separated by a gelatine membrane, with electrodes of one and the same metal in both solutions. The direction of the current produced has indicated in which solution the metal electrode has become the more electronegative by going into solution.

According to a theory proposed by Professor F. Sanford, a metal should go into electrolytic solution the more readily as the metallic ions of the electrolyte are more electropositive. Professor Sanford tested this hypothesis for equimolecular solutions of zinc sulphate and copper sulphate, using four different metals as electrodes. It was found that when both electrodes were of the same metal, the electrode in the copper sulphate solution acted like the copper and the electrode in the zinc sulphate solution acted like the zinc in an ordinary Daniell cell. The investigation described in this paper was for the purpose of testing the hypothesis for a greater number of metals and a large variety of solutions.

The method of procedure was as follows: The base of an ordinary U-tube was filled with a freshly prepared gelatine solution. After this had set, the tube was rinsed in distilled water to remove any free gelatine, and the arms were filled with the solutions to be tested. Without delay, electrodes of similar pieces of the same metal were dipped into the two solutions. The circuit was completed through a sensitive galvanometer in series with 100,000 ohms. The deflection of the galvanometer indicated the direction of the current. The U-tube was so placed in a supporting case that the observer could observe the initial deflection of the galvanometer while dipping the metals into the solutions. A deflection of one centimeter on the scale indicated a potential difference between the cell terminals of .0036 volt.

Solutions of the nitrates, chlorides and sulphates of potassium, sodium, ammonium, barium, calcium, zinc, hydrogen, copper and ferric iron were used. Added to this list were the hydroxides and bromides of potassium and sodium, the iodide of potassium and the sulphate of nickel. The concentration of every solution was one-tenth normal (allowance being made in every instance for the water of crystallization) except in the cases of the sulphates of barium and calcium. Saturated solutions of these salts were used.

Copper, zinc, silver, nickel, cadmium, tin, platinum and bismuth electrodes were used in the course of the investigation, but most of the work was done with the first four mentioned. The direction of deflection was entirely independent of which metal was used for the electrodes, and was determined entirely by the character of the electrolytes.

Before each immersion the electrodes were carefully sandpapered, then rubbed with a clean cloth, so that their surfaces were metallic, not oxidized. The dimensions of the electrodes were roughly as follows: Rods of copper 2 mm. in diameter; nickel .75 mm.; zinc, 8 mm.; tin, 7 mm.; cadmium, 6 mm.; bars of silver 2 mm. × 4 mm. The depth of immersion varied from one to five centimeters. It was observed that though the surface of the nickel electrodes was very much less than that of the other metals, the deflections were often much greater with the nickel electrodes than with the others. Apparently some of the solutions had a tendency to induce a passive condition in nickel.

Records were kept of the deflections due to some two hundred cells. In each case three or more readings were taken of the first deflection with each pair of electrodes used; then the electrodes were reversed in the solutions and three or more readings were taken with the new arrangement. In some cases the solutions were interchanged in the U-tubes, so as to eliminate any possibility of an interaction with gelatine causing the current.

The results of the investigation show that the metals can be arranged in a series in the order in which the presence of their ions in a water solution affects the solution tension of a metal when placed in the solution. Furthermore, this series is the same as the contact electromotive series. That is, if both electrodes be of the same metal, the electrode in the solution which contains the more electropositive ion has the higher solution tension and accordingly corresponds to the zinc electrode, while the electrode in the solution which contains the less electropositive ion corresponds to the copper of the ordinary Daniell cell. The order of this arrangement of the metals was determined to the satisfaction of the writer as follows: potassium, sodium, ammonium, barium calcium, zinc, nickel, hydrogen, copper and ferric iron.

There were a few irregularities in certain solutions. Thus, while metals in KBr, KOH, KCl and KNO_3 showed a higher solution tension than in the corresponding sodium solutions, the reverse was the case with K_2SO_4 and Na_2SO_4. The metals for which this was found to be true were copper, cadmium, zinc, nickel, tin and silver. The position of the NH_4 ion was always below that of the sodium ion in the series, but in the case of the K_2SO_4 solution above mentioned the potassium ion came below the NH_4 ion in the series. This seems to indicate that if the salt used was pure potassic sulphate, the potassium ion acted abnormally in this combination. The salt in question was obtained from the supply room of the Chemistry department, and was not analyzed.

The positions of the barium and calcium ions were not checked as thoroughly as the remaining members of the series.

While zinc was found to be above hydrogen in the series, the initial deflection of the galvanometer rapidly reversed. Also, if the electrodes were not sandpapered before interchanging in the solutions the current reversed when the change was made. Careful cleaning of the electrodes before exchanging them always gave the deflection in the original direction. Exposure to the air or merely rubbing with a cloth did not remove the cause of the reversal. The electrodes with which this reversal of deflection was observed were of copper, silver, nickel and zinc.

Nickel ions are placed above the hydrogen ions in the series, but in this case, as in that of zinc and hydrogen ions, the initial deflection very quickly reversed. With nickel and zinc salts the nickel ions were consistently below the zinc ions in the series, and there was no reversal of the initial deflection. The solution tension of the metals used was found to be always higher in solutions of the acids H_2SO_4, HCl, HNO_3 than in equimolecular solutions of their copper salts.

It is an interesting result that copper, nickel and hydrogen ions in sulphate and nitrate solutions cause the electrode immersed in them to have a higher solution tension than in corresponding solutions of ferric sulphate and ferric nitrate, though iron is usually placed above these elements in the contact electromotive series. This seems to indicate that the ions of ferric iron, at least, occupy the position in the electromotive series usually assigned to passive iron. The same relation between the iron and hydrogen ions was shown with ferric chloride and hydrochloric acid solutions.

It was also found that for the same metallic ion in both solutions the solution tension of the electrodes was determined by the character of the negative ion. Solutions of the chlorides and bromides of potassium and sodium and the iodide of potassium all agreed in showing that the solution tension of a metal is greater in the presence of iodine ions than in the presence of bromine ions, and is greater in the presence of bromine than of chlorine ions.

To test the influence of the concentration of the solutions, cells of copper sulphate and zinc sulphate solutions were thoroughly investigated. The investigation showed that while an increase of concentration of either solution caused a decrease of the solution tension of the metal electrode, this decrease was greater in the case of copper than of zinc ions. When the zinc sulphate solution was very concentrated and the copper sulphate solution was very dilute, the galvanometer deflection was appreciably decreased, but was not reversed.

The results of the investigation seem to the writer to indicate that, in accordance with Professor Sanford's hypothesis, the solution of any of the electrolytes used decreases the specific inductive capacity of the water, but the more electropositive an ion the less it decreases the specific inductive capacity of the water.

Stanford University, Cal.,
May, 1915.

SATURATION VALUE OF THE INTENSITY OF MAGNETIZATION AND THE THEORY OF THE HYSTERESIS LOOP.

BY E. H. WILLIAMS.

RECENTLY, Weiss[1] has shown that an alloy composed of iron and cobalt combined in relative amounts given by the expression Fe_2Co gives a much higher value of the intensity of magnetization than either iron or cobalt taken alone. Furthermore, it has been shown by Mr. D. T. Yensen[2] that the magnetic properties of pure iron can be greatly improved by melting the iron in a vacuum and it was hoped that the magnetic properties of Fe_2Co could be improved by treating it in like manner. The object of the present paper was not only to make a careful study of the saturation value of the intensity of magnetization of Fe_2Co prepared under various conditions but to use the data thus obtained in a test of the theory of the hysteresis loop as developed by J. Kunz.[3]

In his paper, Kunz tests the theory with the data then available. The results show the discrepancy between theory and experiment to be very great. If all quantities involved are obtained from the same sample, the test of the theory will be more satisfactory.

PREPARATION OF SAMPLES.

Iron and cobalt were taken in the proportion indicated by the formula Fe_2Co, melted in a vacuum furnace under pressures varying from 5 mm. to 0.5 mm. Hg, allowed to cool slowly and then forged into long bars from which samples were turned. In most cases enough of the material was taken to make both an ellipsoid and a rod—the ellipsoid for the determination of the saturation value of the intensity of magnetization and the rod for the determination of the hysteresis loop. The hysteresis data were taken by Mr. D. T. Yensen on a magnetic testing apparatus similar to those used by the Bureau of Standards. Mr. Yensen has made a study of the samples from the viewpoint of the engineer. His results are to be published soon in the General Electric Review.

[1] P. Weiss, Compt. Rend., 156, p. 1970, 1913.

[2] D. T. Yensen, Bul. No. 72, Eng. Exp. Sta., Univ. of Illinois, Urbana, Ill.

[3] J. Kunz, Phys. Zeit., XIII., p. 591, 1912.

ELLIPSOIDS.

A great deal of trouble was experienced in making ellipsoids that were accurate. The form of the ellipsoids was tested by projecting an image of the ellipsoid on the figure of an ellipsoid drawn to the desired proportions. Finally the accuracy was tested by comparing the volumes obtained by calculation, using the dimensions of the ellipsoid, with those obtained by immersion in distilled water at known temperature. No ellipsoid was used where the difference in volume differed by more than 2 per cent. and most of them differed by less than 1 per cent. The ellipsoids were about 1.19 cm. in length and about .56 cm. in diameter.

The author wishes to express his thanks to P. Weiss for samples of his material which he kindly sent. This material, when received, was porous and had apparently been melted and cast at atmospheric pressure. One ellipsoid was turned from the material just as received. A second ellipsoid was turned from a portion of the material which had been forged into a small rod, after which the remainder of the sample was remelted in a vacuum furnace under a pressure of .5 mm. of Hg. It was then forged into a rod from which an ellipsoid was turned. The results obtained with these ellipsoids are included in Table I.

The field inside an ellipsoid is uniform and is given by

$$H = H_0 - NI, \tag{1}$$

where H_0 is the external field applied, I the intensity of magnetization, H the resultant field within the ellipsoid and N a constant depending on the dimensions of the ellipsoid.

The field H_0 was produced by a large electromagnet the pole pieces of which were 3.2 cm. apart and bored to receive a glass tube 9 mm. in diameter. On this tube was wound an induction helix. The field, H_0, between the poles of the magnet was calibrated by two methods—by means of a flip coil and with a magnetic balance. The mean of the two calibrations, which differed in no case by more than one half of one per cent., was taken to plot the calibration curve. The intensity of magnetization I was obtained by suddenly removing the ellipsoid from the induction helix between the pole pieces and noting the change of flux as indicated by a ballistic galvanometer. From the constants of the apparatus the value of I could be calculated.

If, in equation (1), NI is greater than H_0, H becomes negative while H_0 and I are still positive, *i. e.*, the field within the ellipsoid is opposite in direction to the field outside. The ellipsoids used in this work were such as to produce this result, so that when a hysteresis loop was taken with one of the ellipsoids a very peculiar S-shaped form was obtained.

Results for I_m.

The results for the saturation values of the intensity of magnetization are summarized in Table I. In this table also, values obtained by other experimenters as well as by the author are given for comparison. Annealing these samples at 900° C. and 1100° C. produced practically no change in the values of I_m. Analysis of the first two samples of Fe_2Co listed in Table I., were made, the first showing 33.36 per cent. Co and the second 33.33 per cent. Co. From these results we see that combining pure iron for which the value of I_m is 1,800, when the iron is melted in a vacuum, with cobalt for which the value of I_m is 1,500 when melted under the same conditions, we obtain an alloy for which I_m is 2,050, or 14 per cent. higher than pure iron itself. Weiss, in the paper referred to above, states that if one takes into account the difference in atomic weight, the temperature at which ferromagnetism disappears and the densities, one finds that at ordinary temperatures ferro-cobalt has a magnetization at saturation 10 per cent. higher than that of iron, so that the extra 4 per cent. is probably due to the fact that the alloy in the present case was melted in a vacuum. This conclusion is sub-

Table I.

Values of I_m ($t = 20°$ C.)

Commercial steel (Williams)	1,751
Swedish wrought iron (Ewing)	1,690
Bessemer steel (.4 per cent. C.)	1,770
Electrolytic iron (melted under pressure of 3 mm. of Hg (Williams)	1,798
Cobalt (1.66 per cent. Fe) (Ewing)	1,310
Cobalt (pure) (Stifler)	1,421
Cobalt (melted under pressure of 1 mm. Hg (about 99 per cent. pure) (Williams)	1,504
Fe_2Co melted under pressure of 3 mm. of Hg without being forged (Williams)	1,791
Same—hand forged (Williams)	1,962
Same—forged with steam hammer (Williams)	1,977
Fe_2Co melted under pressure of 1 mm. of Hg. Forged with steam hammer (Williams)	2,050
Fe_2Co melted under pressure of 0.5 mm. of Hg. Forged with steam hammer (Williams)	2,056
Fe_2Co melted and cast at atmospheric pressure (sample received from P. Weiss) (Williams)	1,752
Same—forged as received (Williams)	1,977
Same—remelted under .5 mm. pressure and forged (Williams)	2,038

stantiated by the difference between the last two results of Table I (material received from P. Weiss). This difference is undoubtedly due to melting under greatly reduced pressure since all other conditions are as nearly equal as it was possible to make them.

Photomicrographs of the first two samples of Fe_2Co given in Table I. are shown in Figs. 1, 2, 3 and 4. Fig. 1 is of the first sample after being forged and Fig. 2 is of the same sample after being annealed at 900° C. and cooled uniformly at the rate of 30° C. per hour. Fig. 3 is of the second sample of Fe_2Co listed in Table I. after the same had been forged and Fig. 4 is the same sample after being annealed at 900° C.

Hysteresis Theory.

In the article by J. Kunz referred to above, the author obtains the following expression for the energy of the hysteresis loop:

$$W = 2I_mH_c^2\left[\frac{1}{H_c\sqrt{\dfrac{I_m}{I_m+I_1+\Delta I_1}}} - \frac{1}{H_1-\Delta H}\right]$$

$$+ I_mH_c^2\Delta H\left[\frac{1}{H_c^2\dfrac{I_m}{I_m+I_1+\Delta I_1}} - \frac{1}{(H_1-\Delta H)^2}\right],$$

where I_m is the saturation value of the intensity of magnetization, H_c the coercive force, I_1 the intensity of magnetization corresponding to the magnetizing field H_1, and where

$$H = H_c\left(1 - \frac{1}{\sqrt{2}}\right)$$

and

$$I_1 = I_m\left[\left(\frac{H_c}{H_1-\Delta H}\right)^2 - \left(\frac{H_c}{H_1}\right)^2\right].$$

According to this theory the hysteresis loss per cycle experienced when the field alternates between the values $+H_1$ and $-H_1$, producing the intensities of magnetization $+I_1$ and $-I_1$, can be calculated directly if one knows the values of I_m and H_c for the material concerned.

As pointed out above, the test given this theory proved very unsatisfactory and seemed to indicate that the theory was of very little practical importance.

It seemed desirable to give the theory a thorough test by the careful determination of the four quantities I_m, H_c, H_1 and I_1 with the same sample. The results for the hysteresis loss, W, calculated and the hysteresis loss, W', as measured from the hysteresis loops are given in

Tables II., III. and IV. Table II. is for a sample of Fe_2Co before being annealed; Table III. for the same sample after being annealed at 900° C.,

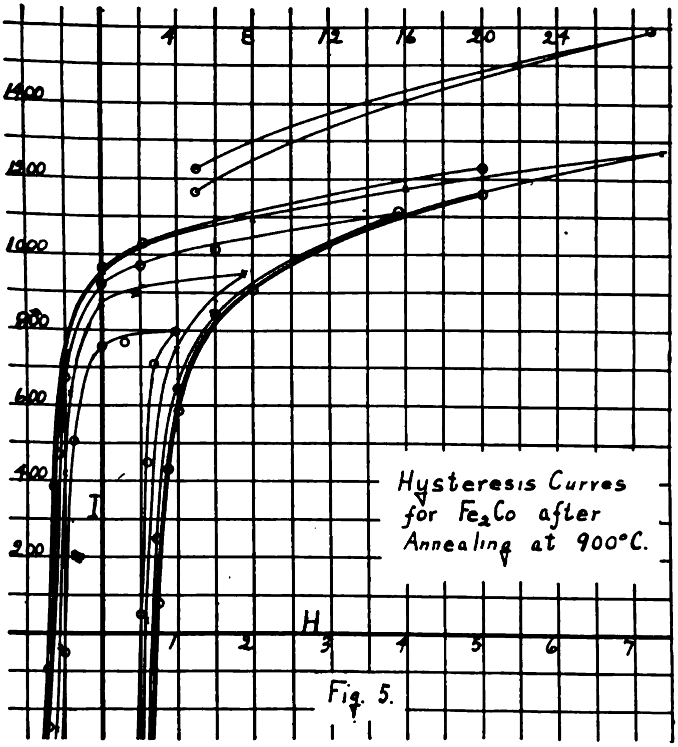

Fig. 5.

and Table IV. for a sample of pure iron after being annealed at 900° C. The hysteresis curves from which the values of W' in Table III. were measured are shown in Fig. 5.

TABLE II.

$I_m = 2{,}050$; $H_c = 6.4$; $\Delta H = 1.876$.

H_1	I_1	ΔI_1	W	W'
14	415	143.5	19,580	18,685
24.5	798	24.2	28,700	28,600
56.5	1,179	2.27	35,620	41,825
146.	1,588	.06	45,630	56,245

The results in Tables II., III. and IV. show fairly good agreement between the values for the hysteresis loss as calculated by the above formula and those obtained by measurement of the hysteresis curves.

If the theory were modified to take into account the curvature as the

PHYSICAL REVIEW, VOL. VI., SECOND SERIES.
November, 1915.

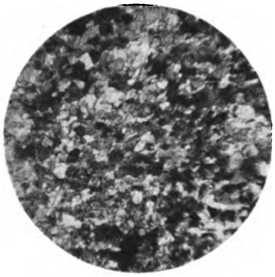

Fig. 1.

Fe_2Co melted under 3 mm. pressure and forged.

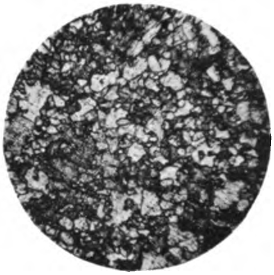

Fig. 2.

Same as Fig. 1, annealed at 900° C.

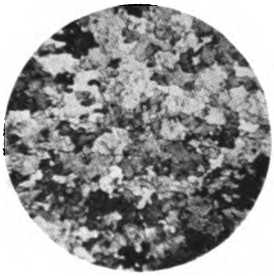

Fig. 3.

Fe_2Co melted under 1 mm. pressure and forged.

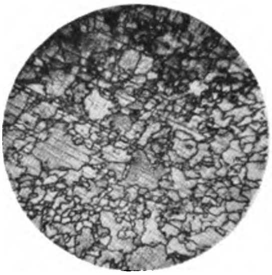

Fig. 4.

Same as Fig. 3, annealed at 900° C.

E. H. WILLIAMS.

Table III.

$I_m = 2{,}050$; $H_c = 0.65$; $\Delta H = 0.19$.

H_1	I_1	ΔI_1	W	W'
.95	796	537.	1,513	1,488
1.82	955	64.4	2,727	2,340
3.82	1,115	6.35	3,434	3,020
7.33	1,273	.902	3,777	3,792
29.	1,590	.013	4,166	4,930

Table IV.

$I_m = 1{,}800$; $H_c = 0.36$; $\Delta H = 0.105$.

H_1	I_1	ΔI_1	W	W'
.6	955	306.	973	970
0.9	1,115	81.	1,364	1,353
1.5	1,195	16.	1,651	1,552
6.5	1,264	.2	1,940	1,918

coercive force is being applied, it would probably agree with experiment even more accurately than it now does. But even as it stands the results for ordinary fields are accurate enough to make the theory of great value in calculating losses where they cannot be measured directly.

Physics Department,
University of Illinois,
May, 1915.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SAN FRANCISCO MEETING.

THE seventy-eighth meeting of the American Physical Society was held at San Francisco, August 2 to 7, 1915. It was a joint meeting with Section B of the American Association for the Advancement of Science. The programs of the meetings on Tuesday, Wednesday and Thursday were in charge of a committee of the Pacific Coast division of the A. A. A. S., of which Professor Fernando Sanford was chairman, and those of Friday were in charge of the Physical Society, President Merritt presiding. The meeting on Wednesday was held at Stanford University, Palo Alto. All other sessions for the reading of physics papers were held at the physical laboratory of the University of California, Berkeley. General sessions of the A. A. A. S. were held in San Francisco.

The following papers were presented:

Tuesday afternoon—Spectroscopy.

(1) A Summary of the Leading Features of Electric Furnace Spectra; (2) The Spectrum of the "Tube-Arc" and a Comparison with Line Dissymmetries in Spark Spectra. ARTHUR S. KING.

Review of Laboratory Studies of the Zeeman Effect, at Mount Wilson Solar Observatory. HAROLD D. BABCOCK.

Pole Effect in the Arc and Its Relation to Other Investigations. CHARLES E. ST. JOHN AND HAROLD D. BABCOCK.

The Efficiency of Astronomical Spectrographs. JOSEPH MOORE.

Wednesday afternoon (at Stanford University).

Discussion and Demonstrations of High Potential Electric Currents. HARRIS J. RYAN.

Thursday forenoon and afternoon—Physics of the Air.

The Thunderstorm. W. J. HUMPHREYS.

New Concepts in Aërology. A. G. MCADIE.

The Application of Physical Principles to Problems Suggested by Oceanic Circulation and Temperatures. GEORGE F. McEWEN.

Radiation and the Atmosphere. C. G. ABBOT.

Solar Radiation and Terrestrial Magnetism. L. A. BAUER.

On the Origin and Maintenance of the Earth's Negative Charge. W. F. G. SWANN.

The Natural Charges of the Elements. FERNANDO SANFORD.

Friday forenoon and afternoon.

Thermo-electric Properties of Alloys of Bismuth and Tin. A. E. CASWELL.

On the Free Vibrations of a Lecher System IV. (By title.) F. C. BLAKE AND CHARLES SHEARD.

Resistance of a Spark Gap. W. P. BOYNTON.

On the Resolving Power of Photographic Plates. ORIN TUGMAN.

Sensitive Moving-coil Galvanometers. FRANK WENNER AND ERNEST WEIBEL.

An Experimental Verification of the Law of Variation of Mass with Velocity for Cathode Rays. LLOYD T. JONES.

The Oxide Resistance Thermometer. S. L. BROWN.

New Form of Radiation Pyrometer. S. L. BROWN.

Electromotive Forces in Isothermal Metallic Circuits. GILBERT N. LEWIS.

A New Method of Determining the Amplitude of Sound Vibrations in Air—with Demonstration. E. P. LEWIS.

An Application of the Koch Registering Michophotometer for Measuring the Sharpness of Photographic Images. ORIN TUGMAN.

Photographic Study of the Tone of the Violin. D. C. MILLER.

The Variation of the Photoelectric Current with the Angle of Emission. WILLARD GARDNER.

A Quantitative Determination of the Earth's Penetrating Radiation. C. H. KUNSMAN.

Ultra-Violet Absorption Spectra. R. L. SEBASTIAN.

The Ultra-Violet Spectra of Krypton and Xenon. E. P. LEWIS.

The Law of Cohesion in Mercury. P. A. ROSS.

Note on the Theory of Ionization by Collision. W. P. ROOP.

Heat Losses from Incandescent Filaments in Air. L. W. HARTMAN.

Magnetic Field Produced by Rotating Solid Conductors in a Magnetic Field. (By abstract.) S. R. WILLIAMS.

Many physicists accepted the invitation to attend a joint meeting of Section A, the American Mathematical Society and the American Astronomical Society, Tuesday forenoon to hear addresses on "The Human Significance of Mathematics," by C. J. Keyser, Columbia University, and "The Work of a Modern Observatory," by G. E. Hale, Mt. Wilson Observatory, Pasadena. Professor Hale's address was illustrated by interesting experiments on vortex motion.

Several instructive demonstrations were arranged by Professor Lewis (some of them at the request of Dr. Hale), where they could conveniently be examined between sessions. Among them were Professor Stebbens' photoelectric cell for stellar photometry; the Zeeman effect with echelon grating, Fabry and Perot étalon, and Lummer and Gehrcke plate; mercury fringes with Fabry and Perot interferometer; the amplitude of sound vibrations made visible by the forced vibrations of lycopodium particles.

Tuesday noon visiting physicists, astronomers, mathematicians and accompanying ladies were the guests of Professors E. P. Lewis, M. W. Haskell and A. O. Leuschner, at the luncheon at the Faculty Club, University of California.

Wednesday evening, immediately after the return from Stanford University, the physicists dined together at Jules Cafe, San Francisco. Attendance about thirty.

During the week many found opportunity to visit the exhibit of the National Bureau of Standards at the Panama-Pacific International Exposition and some to make an excursion to the Lick Observatory at Mt. Hamilton, where the activities of the institution were explained by the astronomers in charge.

At the final session, a hearty vote of thanks was extended to the Pacific Coast Committee for the excellent arrangements made for the meetings, to the authorities of the University of California and of Stanford University for the accommodations provided and especially to the physics staff of the two institutions for the many courtesies extended by them.

A. D. COLE,
Secretary.

Second Series. *December, 1915* *Vol. VI., No. 6.*

THE

PHYSICAL REVIEW.

THE STRUCTURE OF γ RAYS ON THE BASIS OF THE ELECTRO-MAGNETIC THEORY OF LIGHT.

By Jakob Kunz.

THE difficulties in the theories of radiation have become so great in the last few years that only a very fundamental new idea will be able to bring harmony into the present chaos of facts and theories. Before that solving idea appears, we can only draw all the logical conclusions which follow from a given hypothesis and compare these conclusions with experiments. This procedure leads to the result that neither one of the present hypotheses is able to coördinate satisfactorily all the facts. The electromagnetic undulatory theory of light explains the phenomena of reflection, refraction, interference, diffraction, etc., but it fails to explain the phenomena of radiation, the photoelectric and the related effects. The corpuscular theories and the quantum theories on the other hand are especially invented for the explanation of the latter group of phenomena, failing to account for the first group. Not only are the fundamental assumptions of the two theories different, but the older electromagnetic undulatory theory gives not only mathematical relations between the different quantities involved, but it visualizes at the same time, the phenomena, which are explained, so that we can see the mechanism of the processes. The recent quantum theories on the other hand give us only algebraic relations between different quantities such as the law of the photoelectric effect $\frac{1}{2}mv^2 = hn - V_0$, without giving us the least idea as to the mechanism of the phenomenon. It seems to be advantageous if not necessary for a theory to visualize the phenomena. Led by this idea, I shall show by the following figures and calculations that the electromagnetic theory of very hard Roentgen and γ rays leads to conclusions which remind us of an emission or corpuscular theory of rays. The problem has already been solved by A. Sommerfeld,[1] "Uber die Structur der γ Strahlen." I shall use, however, a different method which allows the visualizing of the remarkable conclusion of the electromagnetic theory.

---

[1] Sitzungsberichte der K. B. Akademie der Wissenschaften, 41, p. 1, 1911.

An electron moves with the velocity v in the x direction; the electric force E at a distance r from the charge making an angle φ with the direction of motion is equal to

$$E = \frac{e\left(1 - \frac{v^2}{c^2}\right)\sqrt{x^2 + y^2 + z^2}}{\left[x^2 + (y^2 + z^2)\left(1 - \frac{v^2}{c^2}\right)\right]^{\frac{3}{2}}}.$$

x, y, z are the coördinates of the point in which the electric force E is measured, the zero of the system of the coördinates lies in the electron. We can express E also in the following way

$$E = \frac{e\left(1 - \frac{v^2}{c^2}\right)}{r^2\left(1 - \left(\frac{v^2}{c^2}\right)\sin^2\varphi\right)^{\frac{3}{2}}}.$$

The magnetic force H is given by

$$H = \frac{Ev \sin \varphi}{c}.$$

These equations tell us that with increasing velocity v the electromagnetic field following the electron, is more and more compressed as it were toward the equatorial plane, being perpendicular to the direction of motion.

If now the electron comes into collision with a metallic plate it will come to rest during an interval of time t and move meanwhile over the distance l. If we draw the line of force t seconds after the collision began, we find the well-known disturbance within the Roentgen pulse, whose thickness δ is a function of ϑ given by the equation

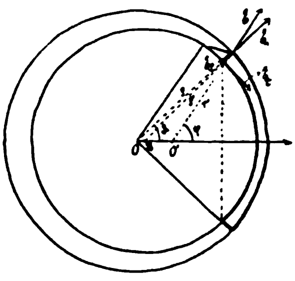

Fig. 1.

$$\delta = \frac{l}{v}(2c - v \cos \vartheta).$$

Within the sphere with radius ρ' drawn round about B of Fig. 1 the final position of rest of the electron, we find the ordinary electrostatic field. Without the sphere with radius ρ, drawn about o, where the collision at the moment $t = 0$ began, we find the electromagnetic field accompanying the electron in motion. The electric force E, pointing toward o' where the electron at the moment t would be, if it had not been stopped, is equal to

$$E = \frac{e(1 - \beta^2)}{r^2(1 - \beta^2 \sin^2 \varphi)^{\frac{3}{2}}}; \quad \beta = \frac{v}{c}.$$

The component En of E in the direction ρ is equal to

$$E_n = \frac{e(1 - \beta^2) r \cos (\varphi - \vartheta)}{r^3(1 - \beta^2 \sin^2 \varphi)^{\frac{3}{2}}},$$

$$r \cos (\varphi - \vartheta) = \rho(1 - \beta \cos \vartheta),$$

$$r^3(1 - \beta^2 \sin^2 \varphi)^{\frac{3}{2}} = \rho^3(1 - \beta \cos \vartheta)^3,$$

$$E_n = \frac{e(1 - \beta^2)}{\rho^2(1 - \beta \cos \vartheta)^2}.$$

We shall now calculate the tangential electric force E_t in the shell. In Fig. 1 we consider the volume cut out of the shell by a cone with an angle ϑ. As there are no charges within this cap, the resultant flux of the electric force flowing out of the volume must be equal to zero. The inflowing flux ϕ_1 is due to the component E_t' and to the force e/ρ'^2 or approximately e/ρ^2

$$\phi_1 = E_t \delta 2\pi\rho \sin \vartheta + \frac{e}{\rho^2} 2\pi\rho(\rho - \rho \cos \vartheta),$$

$$= E_t \delta 2\pi\rho \sin \vartheta + e 2\pi(1 - \cos \vartheta).$$

The outflowing flux ϕ_2 is due to the force E_n and is equal to

$$\phi_2 = \int_0^{\vartheta} E_n 2\pi\rho \sin \vartheta d\vartheta \cdot \rho$$

$$= e(1 - \beta^2) 2\pi \int_0^{\vartheta} \frac{\sin \vartheta d\vartheta}{(1 - \beta \cos \vartheta)^2}$$

$$= e(1 + \beta) 2\pi \frac{1 - \cos \vartheta}{1 - \beta \cos \vartheta}$$

$$\phi_1 = \phi_2,$$

hence

$$E_t \delta 2\pi\rho \sin \vartheta + e 2\pi(1 - \cos \vartheta) = e(1 + \beta) 2\pi \frac{1 - \cos \vartheta}{1 - \beta \cos \vartheta}$$

$$E_t = \frac{e\beta \sin \vartheta}{\delta\rho(1 - \beta \cos \vartheta)} = \frac{ev \sin \vartheta}{\delta\rho(c - v \cos \vartheta)}.$$

In every electromagnetic disturbance the electrostatic energy is equal to the magnetic energy. This is the case if we assume for the magnetic force H in the pulse the expression

$$H = cE_t.$$

The distribution of the lines of force is shown in Fig. 2, and in Fig. 3 for the limiting case where the velocity v becomes equal to the velocity c of light. We see from these figures that with increasing velocity v the electric force E_t becomes a maximum in a certain direction ϑ_m where most of the energy flows away from the electron, and that in the limit for $v = c$ the energy flows out in the direction $\vartheta_m = 0$, that is in the direction of motion of the electron. When the velocity v is so small that it can be neglected with respect to c, then on the contrary, the maximum of the energy radiates away from the electron in the equatorial plane.

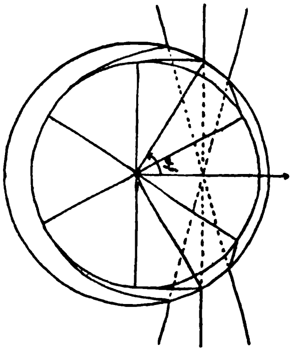

Fig. 2.

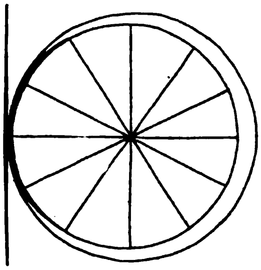

Fig. 3.

$$E_t = \frac{ev^2 \sin \vartheta}{l\rho(c - v \cos \vartheta)(2c - v \cos \vartheta)}.$$

If we neglect at first the change in the factor $1/(2c - v \cos \vartheta)$, we get

$$E_t = \frac{ev^2 \sin \vartheta}{l\rho(c - v \cos \vartheta)}$$

and

$$\frac{\partial E_t}{\partial \vartheta} = \frac{e}{l\rho} \frac{v^2(c \text{ vos } \vartheta - v)}{(c - v \cos \vartheta)^2},$$

which vanishes when $\cos \vartheta = v/c$; for this angle the electric force is a maximum and the energy radiating away from the electron becomes approximately a maximum also.

When $\frac{v}{c} = 0.9$ then $\vartheta = 25° 45'$,

when $\frac{v}{c} = 0.99$ then $\vartheta = 8°$ and when

$\frac{v}{c} = 1$ then $\vartheta = 0°$.

The effect becomes marked only when the velocity v approaches that of light. Returning to the complete expression E_t, we find that it becomes a maximum for the angle ϑ determined by

$$\cos^3\vartheta - 2\left(1 + \frac{c^2}{v^2}\right)\cos\vartheta + 3\frac{c}{v} = 0.$$

For

$$\frac{c}{v} = \frac{10}{9},$$

the three roots are -2.42, 1.497 and 0.9210, hence the angle $\vartheta = 22° 55'$. But as the shell has not everywhere the same thickness, this angle does not accurately indicate the direction in which most of the energy is radiated away.

The energy of the electric force E_t within the elementary volume $2\pi\rho \sin\vartheta\rho d\vartheta\delta$ is equal to

$$dE_{es} = \frac{1}{8\pi}E_t^2 2\pi\rho\sin\vartheta\rho d\vartheta\delta$$

$$= \frac{1}{4}e^2\frac{v^3\sin^3\vartheta d\vartheta}{l(2c - v\cos\vartheta)(c - v\cos\vartheta)^2}.$$

The electrostatic energy in the cap under the angle ϑ is given by the integral

$$E_{es} = -\frac{1}{4}\frac{e^2v^3}{l}\int_0^\vartheta\frac{\sin^2\vartheta d\cos\vartheta}{(2c - v\cos\vartheta)(c - v\cos\vartheta)^2}$$

$$= \frac{1}{4}\frac{e^2}{l}\left\{\frac{3c^2 - v^2}{c^2}\log\frac{c - v\cos\vartheta}{c - v} - \frac{4c^2 - v^2}{c^2}\log\frac{2c - v\cos\vartheta}{2c - v}\right.$$

$$\left. + \frac{c^2 - v^2}{c}\left[\frac{1}{c - v\cos\vartheta} - \frac{1}{c - v}\right]\right\}.$$

The function

$$f(\vartheta) = \frac{\sin^3\vartheta}{(2c - v\cos\vartheta)(c - v\cos\vartheta)^2}$$

or

$$f(\vartheta) = \frac{\sin^3\vartheta}{\left(2 - \frac{v}{c}\cos\vartheta\right)\left(1 - \frac{v}{c}\cos\vartheta\right)^2}$$

has been plotted in Fig. 4 for the values $v/c = 9/10$ and $v/c = 99/100$. This figure shows clearly that with increasing velocity the energy is radiated away in a direction which approaches more and more the direction of motion of the electron. The bearing of this conclusion on the fluctuations of Schweidler and perhaps on the difference in the photoelectric effect according to the incidence of the beam of light, or Roentgen rays is obvious. If we attribute to the electromagnetic field not only energy, but also momentum and mass, then it follows, that the electromagnetic mass of the electron, when it comes to rest, is thrown forward more and more with increasing velocity. This electromagnetic mass and momentum concentrated in a comparatively small space, is not so very different from the notion of light particles in the old emission theory.

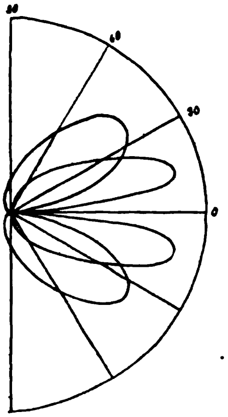

Fig. 4.

University of Illinois,
Laboratory of Physics,
May 22, 1915.

ABSORPTION OF THE β-PARTICLES FROM SOME OF THE RADIOACTIVE SUBSTANCES BY AIR AND CARBON DIOXIDE.

By Alois F. Kovarik.

IT is a well-known fact that the absorption of the β-particles from some of the radioactive substances follows an exponential law, at least over a large part of the absorption curve when the ionization method of measurements is used. It was shown by Kovarik and McKeehan[1] by a statistical method that the numbers of β-particles are not diminished exponentially when the β-particles pass through matter, this, however, does not decrease the value of the ionization method because of its simplicity in application in checking up β-radiations of any radioactive material. In the ionization experiments, the absorbing material used is generally solid material, and usually, aluminium or tin foils. The solid foils can never be obtained uniform in thickness, if thin foils are desired, as, for example, in studying soft β-radiations. It would, therefore, seem desirable to devise a method of investigation of the absorption of the β-particles, by the ionization method, in which the absorbing material would be a gas which would permit uniform layers of absorbing molecules and also give possibilities of use in the cases where layers of relatively few absorbing molecules might be desired. This was done and the exponential law was found verified for gases for the rays for which the absorption curve was exponential for aluminium. A determination of the absorption coefficient was then deemed also desirable; likewise an investigation of the relation of activities of the soft and hard radiations in case of some of the radioactive substances.

The first determination of an absorption coefficient in a gas is due to Eve[2] who obtained a value for the coefficient of absorption of the heterogeneous radium C rays in air. His method consisted in measuring the ionization produced in a β-ray electroscope when the source of radiation was placed at different distances from the electroscope and applying the inverse square law. This method is readily applicable to strong and penetrating radiation where the distances may be so great that the size of the electroscope and the general disposition will affect the results in only a slight manner. He obtained $\mu = .0045$ cm.$^{-1}$ air. Shortly after that, the writer[1] published abstracts of the preliminary work. Since then, a paper on the absorption of the β-particles of uranium in air by Florance[2] has appeared.

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[1] Kovarik, Alois F., and McKeehan, L. W., Phys. ZS., 15, p. 434, 1914.

[2] Eve, A. S., Phil. Mag., S. 6, 22, p. 8, 1911.

In a former investigation[3] of the β-radiations by the writer, it was first pointed out that the soft radiation of Radium *D*, *E*, *F* is most likely due to radium *D*. This was soon confirmed by v. Beyer, Hahn, and Meitner[4] by a photographic method applied to the magnetic spectra. They showed in fact that radium *D* has two line spectra, one corresponding to rays having an absorption coefficient of about 300 cm.$^{-1}$ aluminium and the other very much softer. In the present investigation the method used made it possible to separate these two radiations by studying their absorption curves in air.

METHOD AND APPARATUS.

The method employed is, in fact, the same in principle as that used by Bragg and Kleeman in their study of the ionization curves of the α-particles. An ionization chamber 2 mm. deep (*AB*, Fig. 1) consisting of a circular brass plate 7.4 cm. in diameter, connected electrically by a pair of quadrants of an electrometer, and a thin aluminium foil, 0.003 cm. thick, connected to one end of a high potential battery, whose other end was to earth, was fixed in position. A guard ring in the same plane as the circular plate of the ionization chamber and held rigidly to it by means of amber bridges with a space of 1 mm., helped to form a uniform field in the ionization chamber. The source of β-rays was placed at *D* on a central axis perpendicular to *A* and at any distance not greater than 10 cm. from the ionization chamber. Between the source and the high

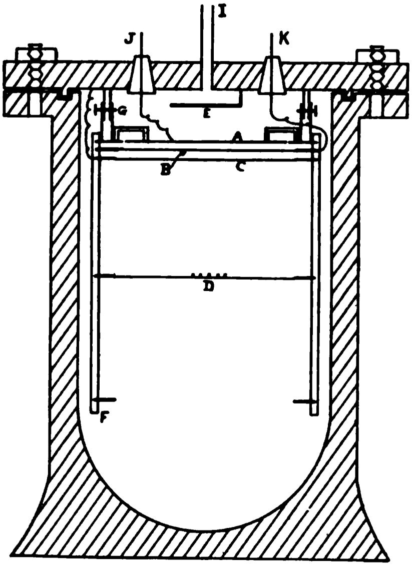

Fig. 1.

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[1] Kovarik, Alois F., PHYS. REV., XXXIV., p. 142, 1912; PHYS. REV., N. S., 3, p. 150, 1914.

[2] Florance, D. C. H., Phil. Mag., S. 6, 25, p. 172, 1913.

[3] Kovarik, Alois F., Phil. Mag., S. 6, 20, p. 849, 1910.

[4] v. Beyer, O., Hahn, u. Meitner, Phys. ZS., 12, p. 378, 1911.

potential plate *B* was another foil (.0003 cm. aluminium) connected to earth, forming an ion trap preventing disturbances should the foils of aluminium have small holes. The foils of *B* and *C* were attached to rigid iron rings which along with the guard ring of *A* were held in position by being set into slits in 3 ebonite rods, *F*. The whole was attached by means of screw connectors, *G*, to the removable cover of the apparatus cylinder for the gas. This cylinder was a strong brass holder 18 cm. deep, and 10 cm. in diameter. The gas entered through *I* from a tank containing the gas at high pressure. A gas manometer consisting of air enclosed in a long (130 cm.) capillary glass tube by a thread of mercury 5 cm. long was in communication. The capillary tube was carefully calibrated and the pressures were deduced by Boyle's law. *E* was a metal shield protecting the ionization chamber from the stream of gas from *I*. The air used was dry, whereas the carbon dioxide was the ordinary commercial product and quite moist. The quadrant electrometer used was of the Erikson-Dolezalek type.[1] On account of the weak material available in some cases and on account of the small volume of the ionization chamber a sensitive instrument was necessary. The Erikson method of charging the needle makes it a simple matter to use the finest quartz fibers available without altering their coefficient of torsion. The sensibility of the instrument used was 2,500 mm. per volt, the scale being 150 cm. from the mirror of the instrument.

In some of the experiments the rate method of observation was employed but on account of varying electrical leaks depending on potential of the charge conveyed to the quadrants, the null method of Townsend[2] was substituted and found far more satisfactory.

The β-particles coming from *D* radiate in all directions and some pass within the frustum of the cone defined by the plane circular source used at *D* and the ionization chamber. The particles are subject to absorption by the gas between *B* and *D* and also by the gas within the ionization chamber itself. If the pressure of the gas in the vessel is increased, the absorbing medium is proportionately increased in quantity but the ionization is also increased. The increase in ionization is, within the pressures used (20 atmospheres), proportional to the pressure. Consequently, the observed ionization currents at the various pressures were reduced to what they would be at one atmosphere. By plotting these values against pressure in atmospheres, one obtains an absorption curve and a coefficient of absorption per atmosphere of the gas used can be deduced for any particular disposition of the source *D*. To compare results, it is necessary to know the depth of the absorbing layer of gas, and since the β-rays are not parallel but radiate in all directions, it is necessary to obtain the mean distance traversed by a β-particle through the gas. Disregarding deflections in its path this distance would constitute the mean path of the β-particles. This distance was obtained graphically very readily, the ionization chamber being circular, the source being also circular and symmetrically placed below the chamber. Since the gas in the ionization chamber also absorbs the radiation, the measurements were made to a plane midway between the plates of the ionization chamber. The coefficient of absorption could then be deduced in cm.$^{-1}$ or (gm. per cm.^{2})$^{-1}$ of the gas used.

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[1] Erikson, H. A., Phys. Rev., N. S. 1, p. 253, 1913.

[2] Townsend, J. S., Phil. Mag., S. 6, 6, p. 598, 1903.

It is to be noted that the potential difference between *A* and *B* must be sufficient for a saturation current. For the distance of 2 mm. between *A* and *B*, 2,000 volts is sufficient for the pressures used.

Since the β-particles are readily deflected in their course, and considerably reflected by brass, some rays might enter the ionization chamber by a roundabout way. To prevent such reflected rays having effect in this manner a cylinder of paper, which reflects[1] only a small percentage of the incident radiation, was wrapped around the ebonite rod *F* before inserting the apparatus into the vessel. The effect of the incident radiation then became negligible.

With the entrance of a gas into the vessel a charging up of the amber insulation plugs took place and time had to be allowed before consistent readings could be taken. This was, of course, a source of annoyance especially in the case of rapidly disintegrating substances.

The absorbing value of the thin aluminium foil *B* and *C* had to be taken into consideration in the case of soft rays. The natural leak of the apparatus at different pressures was obtained and readings with the rays were properly corrected.

RESULTS.

It was first shown that the radiations which are absorbed exponentially by aluminium are also absorbed exponentially by gases. The curves of Fig. 2 show the result for the rays of radium *E* absorbed by air and carbon dioxide, the mean path being 10.4 cm. These logarithmic curves show perfect resemblance to similar curves with aluminium, which are well known. The same thing was found with the other radiations investigated, all giving a straight line for that part of the logarithmic curve which was found to obey the exponential law with aluminium absorbing foils.

In order to see whether the mean path obtained graphically is correct, observations were made on the absorption coefficient of the β-rays from radium *E* when the source was placed at different distances from the ionization chamber. The results are given in Table I., where the coefficients of absorption expressed per cm. of air are entered against the mean path obtained graphically. The agreement is good except for the shortest path in which case the rays varied much in the length of path.

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[1] Loc. cit.

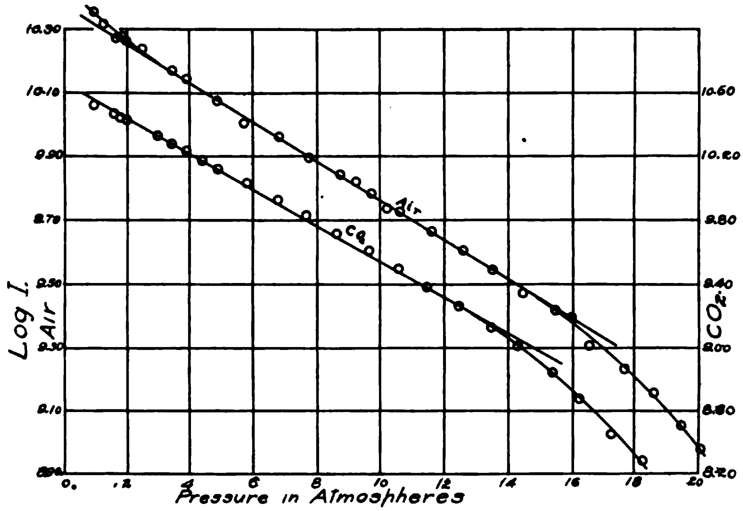

Fig. 2.

TABLE I.

Radium D, E, F at Different Distances from the Ionization Chamber.

Mean Path of the β-Particles in Cm. of Air.	Absorption Coefficient in Cm.$^{-1}$ Air at 1 Atmosphere and 22° C.
10.60	0.0151
5.36	.0145
3.00	.0149
2.31	.0150
1.64	.0160

The radioactive substances used were radium *D*, *E*, *F*, one specimen chemically separated and another prepared from radium emanation. These gave the radiations from radium *E* and also from radium *D*. The actinium active deposit on thin aluminium was used for actinium *B* and *D*, and thorium active deposit for thorium *B* and $C + D$. Uranium *X* chemically separated and also uranium oxide were used for the soft and hard rays of UX_1 and UX. The soft radiations were separated from the hard radiations by subtracting the latter from the observed results, calculating their values for low pressures according to the exponential law. There was no difficulty in doing this when observations were carefully carried through with small pressures and when the mean path was short. The results are given in Table II., in which the values of the coefficients are expressed for air and carbon dioxide both in cm.$^{-1}$ at one atmosphere and 22° C. and also in (gm./cm.^{2})$^{-1}$.

TABLE II.

Coefficient of Absorption.

Source of β-Particles.	Cm.$^{-1}$ Air 1 Atm. and 22° C.	Air (Gm./Cm.^{2})$^{-1}$.	Cm.$^{-1}$ CO_2 1 Atm. and 22° C.	CO_2 (Gm./Cm.^{2})$^{-1}$.
Radium E	.0152	12.70	.0297	16.31
Actinium C+D	.0091	7.60	.0175	9.62
Thorium C+D	.0068	5.68	.0129	7.08
Uranium X_2	.0065	5.43	.0114	6.26
Uranium X_1	.12	100.	.23	126.
Radium D	.097	81.	.183	101.
Radium D (very soft)	.64	535.	1.69	930.
Thorium B	.090	75.	.142	78.
Actinium B	.31	260.		

In order to obtain an idea of the relative ionizations produced by soft and hard rays when both are present, extrapolation exponentially to zero thickness of the absorber was carried out, and the ratio of the ionization produced by the soft rays to that produced by the hard rays in air at one atmosphere was averaged for the particular radiations in the various experiments. These values are given in Table III. It will be noted that the value for the soft thorium radiation compared with the hard is higher than that usually given. The value for the very soft radium *D* radiation must be taken with reserve, because the extrapolation was too great, but that for the more penetrating radiation of radium *D* seems satisfactory; the same is true of the relation of the soft to the hard radiation of actinium active deposit.

TABLE III.

Relation of Ionizations in One Atmosphere of Air of Soft Radiations to Hard Radiations Reduced by Extrapolation to Zero Absorber.

Sources of β-Particles.	Ratio of Ionizations.
$\frac{\text{Radium D}}{\text{Radium E}}$ (more penetrating)	0.30
$\frac{\text{Radium D}}{\text{Radium E}}$ (very soft)	2.4(?)
$\frac{\text{Actinium active deposit (soft)}}{\text{Actinium active deposit (hard)}}$	1.14
$\frac{\text{Thorium active deposit (soft)}}{\text{Thorium active deposit (hard)}}$	2.86

CONCLUSIONS.

1. A method depending on the change of pressure of a gas was devised for measuring the absorption of the β-particles. This consists of measuring the ionization in a shallow ionization chamber placed at a fixed distance from a source of radiation within a high pressure vessel: reducing the ionization readings at various pressures to that at one atmosphere of pressure, measuring graphically the mean path of the β-particles, and then, in the usual manner, deducing the coefficient of absorption.

2. It was shown that the absorption curves in gases are the same in shape as those obtained with aluminium foils.

3. It was shown that the graphical method of obtaining the mean path is correct.

4. Values of the absorption coefficients in air and carbon dioxide of the β-particles of some of the radioactive substances were obtained.

5. Relation between the ionizations of the soft and the hard radiations were computed by extrapolation to zero absorber. This was done for the two soft radiations of radium *D* compared with the effect of the radiations of radium *E*; soft and hard rays of the actinium active deposit; soft and hard rays of the thorium active deposit; soft and hard rays of uranium *X*.

In conclusion I desire to express my deep gratitude to the committee of the Minnesota Research Fund for allowing funds to procure some of the necessary apparatus and material to carry out this work.

Physical Laboratory,
The University of Minnesota,
June 11, 1915.

DISTRIBUTION OF TRANSMITTED AND REFLECTED β-PARTICLES DETERMINED BY THE STATISTICAL METHOD.

By Alois F. Kovarik and L. W. McKeehan.

THE scattering of cathode and β-particles has been studied by a number of investigators. Villard[1] observed the separation of β from γ rays by the scattering of the former, using a photographic method. Crowther[2] obtained "complete" scattering of β-rays from uranium by aluminium 0.015 cm. thick or gold 0.0002 cm. thick. This refers to the thickness beyond which the absorption of an originally parallel beam of rays became exponential. Kovarik[3] showed the importance of scattering in measurements of absorption with different experimental dispositions. Wilson's[4] photographs of the tracks of cathode and β-particles show the scattering of individual particles. McKeehan's[5] work on the scattering of cathode rays in air showed the presence of single scattering in the case of rays much slower than β-rays. Scattering was proposed by us[6] to explain certain initial peculiarities in curves for combined absorption and reflection of β-rays.

The theory of single scattering of an electrified particle given by Rutherford[7] and experimentally verified by Geiger[8] in the case of α-particles, seems the most probable basis for any explanation of the scattering of β-rays, including under this term all changes from the original direction of projection.

Measurement of the number of β-particles distributed in any direction by a plate of metal placed in the primary beam, should afford a test for any such explanation. By the statistical (or counting) method here employed, such numbers are obtained directly, and should be more conclusive than numbers deduced by interpreting the results of ionization experiments.

[1] Villard, P., Ions, Electrons, Corpuscles, p. 1024, 1905.

[2] Crowther, J. A., Proc. Roy. Soc., A 80, p. 186, 1908.

[3] Kovarik, Alois F., Phil. Mag., S 6, 20, p. 849, 1910.

[4] Wilson, C. T. R., Proc. Roy. Soc., A 87, p. 277, 1912.

[5] McKeehan, L. W., Phys. Rev., N. S. 4, p. 140, 1914.

[6] Kovarik, Alois F., and McKeehan, L. W., Phys. ZS., 15, p. 434, 1914.

[7] Rutherford, E., Phil. Mag., S 6, 21, p. 669, 1911.

[8] Geiger, H., Proc. Manch. Lit. and Phil. Soc., 55, Pt. II., p. xx, 1911.

Apparatus and Manipulations.

In our previous paper[1] we described the general method here employed. Certain alterations adapting the method to the experiments in hand were found necessary. In order to obtain the distribution of the rays in azimuth, a source of β-rays and a square radiating plate 6 cm. on the edge could be fixed in any desired positions relative to each other, and then could be rotated as a whole about an axis lying in the radiating plate. Two cylindrical counting chambers were fixed in position facing each other, and the axis of rotation bisected their common axis so that simultaneous readings could be taken of the numbers emitted from the radiating plate on the side of transmission and on the side of reflection. The apparatus was made especially rigid and accurate in its working parts. Each counting chamber consisted of a brass tube of inside diameter 1.3 cm. and 7.5 cm. long. Two diaphragms each having a central opening 0.165 cm. in diameter were fixed 1 cm. apart in this tube making the depth of the counting chamber 2.3 cm. The remainder of the tube in front of the first diaphragm formed a shield to exclude extraneous rays and was beveled on one side so that the inner surface would not be exposed to direct radiation from the source with consequent large reflection. The chambers with their points were interchangeable. All metal surfaces exposed to the rays, and from which it might be possible for particles to reach either counting chamber by reflection, were covered with cardboard 0.3 cm. thick.

Discharging points of steel and of platinum were used. In the case of platinum the most satisfactory points were obtained by momentarily heating in a flame the tip of a short piece of platinum wire 0.005 cm. in diameter, set in a brass rod. The platinum fused into a beautifully smooth knob, the size depending upon the heat applied and its duration, and by suitable manipulation a much smaller knob could be produced at the extremity of the first. Such a point, if symmetrical, gave excellent results, but continued use caused disintegration of the surfaces and the destruction of the point. Contrary to the experience of Chadwick[2] a more permanent point could be obtained by grinding a hard steel sewing needle to an exceedingly tapering cone which was then heated to redness in an alcohol flame. The resulting surface was smooth and less affected by use than that of the platinum points.

To avoid the errors due to gradual change in the conditions of discharge from the points they were placed at frequent intervals in a standardizing counting chamber of fixed dimensions and distance from a source of α-

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[1] Loc. cit.

[2] Chadwick, J., Verh. d. D. Phys. Ges., 16, p. 383, 1914.

or β-rays. The standard sources used were, for the α-rays, a polonium plate, and for the β-rays, a radium *D*, *E*, *F* plate. The number of α-particles emitted by the polonium plate was checked by the electrical and scintillation methods. The number to be expected by the statistical method was then calculated, and points giving values in good agreement with this were considered to be in good working condition if no regularity in sequence or grouping of the deflections in the electrometer (*e. g.*, double deflections) could be noted, and if the individual deflections were uniform in size and fairly large. Two standards were used because the first effect of deterioration was noticeable with β-rays. Faulty points give high values firstly, because discharges occur without the presence of rays and secondly, because a single particle causes a series of two or three discharges in quick succession. The β-ray standard was fixed to give about 30 particles per minute in the counting chamber and at this rate the occurrence of double deflections should be rare; hence the occurrence of many "doubles" in this standardization gave good grounds for rejection of the point.

Points which satisfy these tests do so over a range of applied potential difference of more than 50 volts in a total of 1,500 volts, the exact range and maximum depending upon the point. With all these precautions the method is highly satisfactory, contrary to the conclusions of certain other investigators.[1]

Two string electrometers of the Lutz-Edelmann type, one connected to each discharging point, were used for visual observation, the sensibilities being adjusted to be approximately equivalent. The electrometer fibers were 0.0006 cm. in diameter. The general disposition of electrical con-

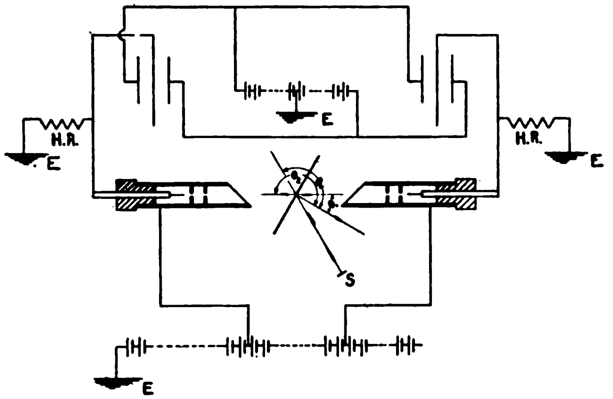

Fig. 1.

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[1] Myssowsky, L., and Nesturch, K., Ann. d. Phys., 43, p. 461, 1914.

[2] Loc. cit.

nections was the same as in our previous work[2] so modified as to permit the use of different potentials on the two counting chambers when the points required this difference. The apparatus and connections are shown in diagram in Fig. 1.

RESULTS.

The number of particles entering the counting chamber per minute was obtained for each of the values of θ shown in Fig. 2, in which the normal to the radiating plate on the same side as the source is taken as the line of reference. It is to be noted that in reality this plate and the source were rotated while the counting chambers remained at rest. A series of counts with frequent interchange of points, counting chambers, and angles, was taken until the aggregate time of counting for each position was long.

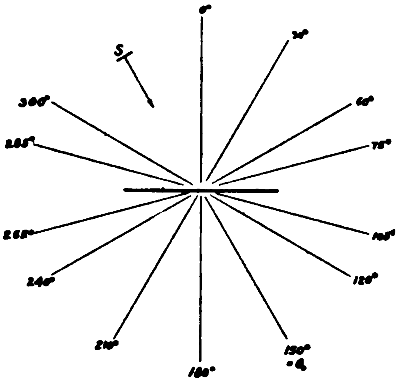

Fig. 2.

The weakness of the available source, a radium *D*, *E*, *F* plate, made it necessary to use small dimensions and a non-parallel beam of rays incident on the radiating plate. The difficulty of calculating the numbers to be expected on certain assumptions regarding the distribution on emergence, to be used in comparison with the experimental results, is unfortunately much increased by this fact, but the corrections for air scattering and absorption become relatively less important. Readings at or near a grazing emergence were omitted because the plate in these positions does not cover the base of the cone defined by the diaphragms of the counting chambers. The thickness of the radiating plate (.0856 gm. Al per cm.^{2}) was selected for two reasons: firstly, this thickness makes the numbers of β-particles emitted from the two sides approximately equal; secondly, this thickness is much greater than the thickness given by various investigators as that necessary for "complete" scattering. The results

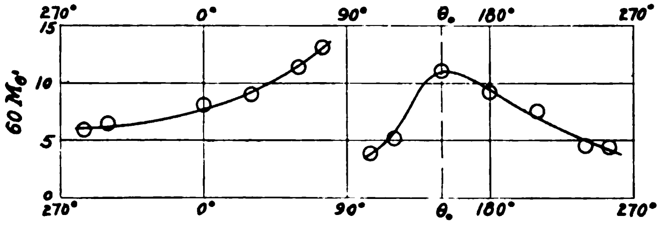

Fig. 3.

obtained in the experiment are shown in Fig. 3. Angles between 270° and 90° correspond to reflection, angles between 90° and 270° to transmission, according to the usual meaning of these terms.

Similar curves for reflection only were obtained with a less rigid form of apparatus using thick and thin plates of tin and a thick plate of carbon, respectively, the dissymetry in the curves being more marked for the thinner or lighter plates.

Curves for transmission through aluminium plates of different thicknesses are shown in Fig. 4, the same variables being plotted as in Fig. 3,

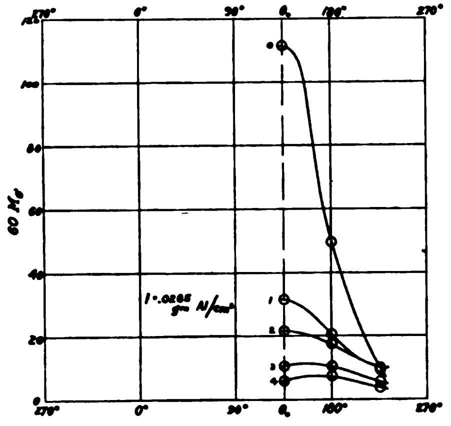

Fig. 4.

but the positions of the source and counting chamber being different as indicated. The suppression of the maximum in the original direction of the beam of rays is very noticeable.

DISCUSSION AND EXPLANATION.

The path in air between large deflections of β-particles, as suggested by Wilson's photographs[1] of their tracks, agrees in order of magnitude with the air equivalent of the thinnest aluminium foil (.0008 gm. Al per cm.^{2}) used in our previous work, which gave a marked scattering effect. This suggests single scattering as the cause of the effect noted, meaning by single scattering the deviation in direction of a β-particle due to a single charged center. We shall assume such single scattering to be the chief cause of the distributions observed above. The gradual curvature of path, perhaps due to the simultaneous action of many central forces, and also shown in the photographs above mentioned, is not excluded by this hypothesis, but is regarded as of secondary importance in determining the final distribution in direction.

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[1] Wilson, loc. cit.

Assume that β-particles of velocity v_0 are incident upon a plate of matter of thickness t and of indefinite extent. We wish to know the probable distribution of the emergent β-particles in any plane perpendicular to the plate.

Let $n_0 d\omega$ be the number of particles incident per second upon a unit area of the plate in directions lying within a small cone of solid angle $d\omega$ the axis of which, produced through the plate makes an angle θ with the normal to the plate on the side of incidence. The total number of particles incident per second upon unit area, or

$$N_0 = \int n_0 d\omega.$$

Similarly, let $n_1 d\omega$ be the number of particles moving in directions lying within $d\omega$ after their first deflection, at whatever depth this occurs. The total number of particles deflected at least once of those incident per second upon unit area, is

$$N_1 = \int n_1 \, d\omega.$$

Extend this notation up to m deflections. The distribution n_m is a function of n_0, v_0, and t. Also $N_{m+1} < N_m$ since some particles included in N_m escape from the plate without suffering a further deflection, and some are stopped completely. Denote the number escaping by N_m', their distribution with angle by n'_m, and let n be the distribution of all the rays escaping from the plate, then

$$n = \sum_{m=0}^{m=\infty} n_m'.$$

Now let $n_m' = a_m n_m$ in which the factor a_m, which must be less than unity, depends upon the following variables:

1. The distribution within the thickness of the plate of the location of the mth deflection; this in turn is a function of m, n_0, v_0, and t

2. The velocity v_m of the rays after the mth deflection; this in turn is a function of m, v_0, and also of θ when m is small

3. The value of θ. The thickness of material traversed after the mth deflection is a function of θ and is least when $\theta = 0°$ or $\theta = 180°$.

The effect of the first variable may be estimated in a few cases. Let the mean depth of the mth deflection measured from the incident side be $\bar{d}_m$. The following relations are obvious.

$$\lim_{t \doteq 0} \bar{d}_1 = \tfrac{1}{2}t,$$

$$d_m > d_{m-1},$$

and

$$\lim_{m \doteq \infty} \frac{\bar{d}_m}{\bar{d}_{m-1}} = 1,$$

for all values of t.

The value of a_m cannot depend upon $\bar{d}_m$ alone but rather upon the distribution of the mth deflections, as a function of the depth, say d_m, but in general an increase in $\bar{d}_m$ will increase a_m on the side of transmission and decrease a_m on the side of reflection.

The effect of the second variable, v_m, is to make a_m decrease as m increases because velocity is reduced by deflections.

The effect of the third variable, θ, is of the same nature as the effect upon the intensity of luminous radiation received from an incandescent plate viewed obliquely, and is due to the absorption of a volume radiation in the material of the radiator. If the plate is thick enough to deflect a number of times practically all the rays that fall upon it, the law of emergence as far as this variable is concerned is identical with that for luminous radiation from a solid and we may put

$$a_m = b_m \cos \theta,$$

in which b_m depends on θ only if n_0 or v_m do so, thus affecting the first two variables discussed above.

The volume radiation here described is in sharp contrast to the surface radiation and consequent uniform distribution due to a thin film of radioactive material, such as radium active deposit.[1]

Substituting the value of a_m in the expression for n we may write

$$n = \cos \theta \sum_{m=0}^{m=\infty} b_m N_m \left(\frac{n_m}{N_m}\right),$$

wherein n_m/N_m depends only upon m, n_0/N_0, and upon the law of scattering while b_m and N_m depend also upon t, and in the general case the former may depend upon θ. In the apparatus actually employed, however, θ_0 varied between very narrow limits at any point of the plate, since the source was small in area, and we may then safely assume that $b_m N_m$ is here independent of θ though not independent of θ_0.

Since a similar sum will express the emergent rays for any value of v_0 we may assume the coefficients to correspond to any initial distribution of velocities. The emergent rays are necessarily heterogeneous in any case.

The number of particles entering the counting chamber per second when it is placed at the angle θ', measured at the center of the plate, is the surface integral

$$M\theta' = \int n\Omega d\sigma = \int N_0 \left(\frac{n}{N_0}\right) \Omega d\sigma,$$

in which Ω is the small solid angle at the surface element $d\sigma$ within which the path of an emergent particle must lie in order that it may enter the counting chamber. The angle Ω and the inclination of its axis to the normal, θ, which determines the appropriate value of n, depend only upon θ', the position of $d\sigma$, and upon the dimensions of the apparatus.

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[1] Rutherford, E., Phil. Mag., S6, 12, p. 152, 1906.

Preliminary experiments showed that N_0 varied inversely as the square of the distance from the source to $d\sigma$ except for the absorption of the intervening air and directly as cos θ_0, within the region to be used.

Values of $M_{\theta'}$ were calculated for the experimental dispositions of source, plate, and counting chamber, and for the following different assumptions regarding the distribution of emergent particles

$$\frac{n}{N_0} = k, \frac{n}{N_0} = k' \cos \theta, \quad \frac{n}{N_0} = k'' \cos^2 \theta.$$

More general distribution laws were not chosen because of the fact that for each of those tested the final results were as well expressed by the simple relation $M_{\theta'} = n/\cos \theta'$, where n corresponds to the value of θ', as by the integral actually used in the extended computations. Calculation also shows that the principal contributions to $M_{\theta'}$ are from a small area near the center of the plate.

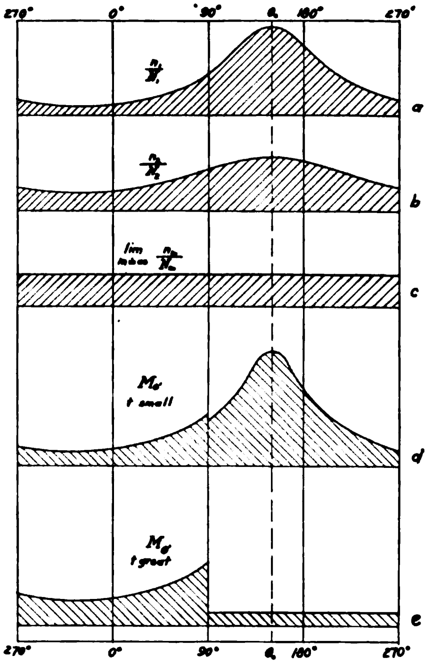

Fig. 5.

Upon the results of these computations we therefore base the following equation as a first approximation

$$M_{\theta'} = \sum_{m=0}^{m=\infty} b_m N_m \left(\frac{n_m}{N_m}\right).$$

The approximation is still closer if the distribution is symmetrical about the normal to the plate.

Experiments to be quoted below make it probable that the mean angle of deviation at a single deflection is fairly large. Assuming this we may predict the approximate shape of the curves connecting n_1/N_1, n_2/N_2, $\lim_{m \doteq \infty} n_m/N_m$, and θ if the incident beam consists of parallel rays.

Such distribution curves are sketched in Fig. 5 (a, b, and c). The maximum remains at θ_0 but becomes less marked as m increases.

Consider the variations in value of the coefficients $b_m N_m$ as t increases from 0 to ∞, and the effect upon $M_{\theta'}$ of these variations. For small values of t the values of N_m form a rapidly diminishing and convergent series. The values of b_m are nearly equal to unity for small values of m; they decrease with increasing m on account of the corresponding decrease in velocity; on the transmission side they increase slightly with increasing m and $\bar{d}_m$, and on the reflection side they decrease slightly with increasing m and $\bar{d}_m$. On the whole we may put

$$M_{\theta'} = \bar{N}_0 \left\{ (1 - c)\frac{n_0}{N_0} + c\frac{n_1}{N_1} \right\},$$

in which c is small compared to unity. Such a distribution is shown by Fig. 5 d. For large values of t the values of N_m diminish less rapidly than above, but the series is still convergent. On the reflection side the values of b_m decrease with increasing m as above, but more rapidly, since $\bar{d}_m$ increases to a greater limiting value than in that case. More terms must be taken before it can be assumed that the sum of the remaining terms is negligible, and since each term so taken follows more nearly a uniform distribution the only change from the previous case is seen in a raising of the whole curve without much change in its shape. On the transmission side the values of b_m increase as m increases (until the increase in $\bar{d}_m$ is overcome by the decrease of v_m), and at first more rapidly than N_m decreases, so that terms for either low or high values of m are less important than some of the intermediate terms. This justifies the equation

$$\lim_{t \doteq \infty} M_{\theta'} = c'\bar{N}_0,$$

where

$$\lim_{t \doteq \infty} c' = 0,$$

expressing a uniform and finally vanishing distribution on the transmission side. Such distributions are shown by Fig. 5 *e*. The experimental curve for $M_{0°}$ (Fig. 3) is seen to be intermediate in character between the curves of Fig. 5 *d* and *e*.

If the distribution, n_0, is similar to that at a point near a thin plane source of radioactive material, b_m will depend on θ and a more general reasoning than that given above must be employed. Let the plate be so thin that the probability of even a single deflection is very small for rays incident normally. For rays incident obliquely, however, the probability of a deflection is greater and some of the deflected rays emerge normally. This means that the number emergent normally from such a very thin foil is greater than the number incident normally. The thickness producing this effect is of the same order of magnitude as the mean free path of the β-particles in the material, and the observed rise will be the more marked the greater is the average deviation at a single deflection. For somewhat greater thickness the original uniform distribution will nearly reëstablish itself, but this will be replaced at still greater thickness by the cosine distribution due to volume emission. If the stoppage is small, as in aluminium, this may correspond to a second maximum in $M_{180°}$ reached more gradually than the first.

Exactly these effects are seen in the case of combined absorption and reflection of β-particles in our previous work,[1] when the absorbing (or scattering) foils were placed in the incident beam close to the source. The sharp initial rise, subsequent drop, and further gradual rise are due to the variations in the number of rays received near the center of the reflector (and therefore near the normal to the absorbing foils). The thickness of aluminium causing the maximum initial rise was 0.0006 cm., so that the "free path" of these β-particles in aluminium is of this order of magnitude. We deduced about the same value from Wilson's photographs of the β-particle tracks in air, by application of the density relation. In the lower curves of the figure referred to above, the second maximum does not appear for the absorbing foils in the reflected beam, because an approximate cosine distribution has already been produced by the reflection. The initial rise is also much reduced for the same reason.

Conclusions.

1. The statistical method of Geiger has proven satisfactory for accurate work on β-radiations with proper methods of experimentation and checks upon the results.

2. This method has been applied to the simultaneous determination of

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[1] Kovarik and McKeehan, loc. cit., see Fig. 6.

the distribution of the particles from radium *D*, *E*, *F* transmitted and reflected by a plate of aluminium of medium thickness.

3. These results and those given in a previous paper have been interpreted in accordance with Rutherford's theory of single scattering.

4. The rays from a thick radiating plate emerge on the transmission side in a manner similar to the emission of light from a heated solid, *i. e.*, according to a cosine law.

5. From the phenomenon of initial scattering described in a former paper we have deduced that the mean path for these β-particles between deflections in aluminium is of the order of 10^{-8} cm.

In conclusion we desire to express our appreciation of the financial assistance afforded us under the provisions of the Minnesota Research Fund.

PHYSICAL LABORATORY,
THE UNIVERSITY OF MINNESOTA,
June 11, 1915.

A METHOD OF MEASURING HEAT CONDUCTIVITIES.[1]

By R. W. King.

UNDER the boundary conditions

$$\theta(0, t) = \theta_1 + \theta_2 \cos \omega t,$$

$$\theta(\infty, t) = 0,$$

the solution of the differential equation

$$\frac{\partial \theta}{\partial t} + \mu\theta = k\frac{\partial^2 \theta}{\partial x^2}, \qquad (1)$$

expressing the linear flow of heat is

$$\theta(x, t) = \theta_1 e^{-p_1 x} + \theta_2 e^{-p_2 x} \cos (\omega t - qx + e), \qquad (2)$$

in which

$$p_1 = \sqrt{\frac{\mu}{k}},$$

$$p_2 = \frac{1}{k}\sqrt{\frac{\mu + \sqrt{\mu^2 + \omega^2}}{2}},$$

$$q = \frac{1}{k}\sqrt{\frac{-\mu + \sqrt{\mu^2 + \omega^2}}{2}}.$$

In these equations k is the ratio of the thermal conductivity to the product of density and specific heat, and μ is a term giving the rate of radiation from the surface of the specimen considered. From the value of q it follows that the velocity of propagation of the heat wave represented by equation (2) is a function of the thermal conductivity, density, specific heat, the period $2\pi/\omega$ of the impressed temperature variation, and the rate of radiation from the surface of the rod. Of these five factors, the only uncertain one is the last; and this can be readily eliminated and the conductivity found if the velocities corresponding to two separate periods are known. We have, calling v the velocity of propagation of the heat wave, λ its wave length and T its period,

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[1] The method of measuring heat conductivities which is described in the following pages is, it is thought, original. It however bears a certain resemblance to the methods of Ångström and Neumann, and it also appears from a recent article by T. Barratt (Proc. Phys. Soc. London, p. 347, 1914) that in some of the experimental features, the present method is similar to his. This however is a coincidence.

For an excellent summary of practically all the various methods of measuring thermal conductivities and for a very complete bibliography the reader is referred to Chwolson's Traité de Physique.

$$v = \frac{\lambda}{T} = \frac{2\pi}{Tq},$$

whence

$$v^2 = \frac{8\pi^2 k}{T^2(-\mu + \sqrt{\mu^2 + \omega^2})}$$

or

$$\mu = \frac{\omega^2 v^2 T^2}{16\pi^2 k} - \frac{4\pi^2 k}{T^2 v^2}.$$

Hence, if, for a constant value of μ, the velocities v_1, v_2 correspond to the periods T_1, T_2 respectively, then

$$\frac{\omega_1^2 v_1^2 T_1^2 - \omega_2^2 v_2^2 T_2^2}{16\pi^2} = 4\pi^2 k^2 \left(\frac{1}{T_1^2 v_1^2} - \frac{1}{T_2^2 v_2^2} \right)$$

and

$$k = \frac{1}{4\pi} \left(\frac{T_1^2 T_2^2 v_1^2 v_2^2 (v_1^2 - v_2^2)}{T_2 v_2^2 - T_1^2 v_1^2} \right)^{1/2}.$$

The following is an account of some experimental work undertaken with the idea of reproducing the conditions of the problem just outlined.

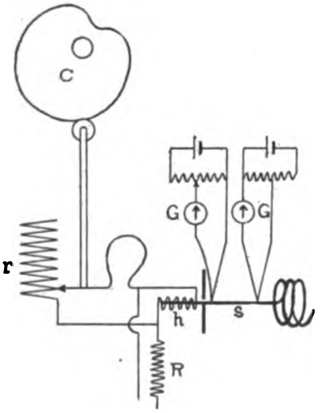

Fig. 1.

The essential parts of the apparatus are shown in Fig. 1. The specimen S is in the form of a wire, usually about 2.5 mm. in diameter and from 25 to 50 cm. in length. The greater portion of this wire is coiled up so that, all together, it occupies a space about 7 cm. long. One end of the specimen is inserted in a small resistance coil h which serves to supply heat to it. The coil h is connected in multiple with a variable resistance r, the two being attached through a larger resistance R to a steady source of current (in the present case, 110-volt D.-C. mains). The value of r is varied by the cam C in such a way that the current I through h is given by the expression

$$I = I_0 \left| \sin \frac{\omega}{2} t \right|.$$

(The design of the cam will be discussed in detail later.) To measure the velocities at which the impressed waves of heat travel along the specimen, two thermo-elements are attached a few centimeters apart to the end of the specimen at which heat is supplied. Each element is in series with a short-period galvanometer and a counter electromotive force equal to the mean value of the electromotive force of the element. By means of this arrangement, the motions of the galvanometers correspond to the variations of the temperatures of the points *a* and *b* from their respective mean temperatures; and to determine the velocity of wave propagation it is only necessary, knowing the distance between *a* and *b*, to determine by observation the time-lag between the motions of the galvanometers.

II. Details of the Apparatus.

The Specimen.—Exact dimensions of the specimens used will be found among the data. In the case of the specimen of tin, the thermo-junctions were between the tin itself and No. 40 constantan wire fused into its surface; and in the case of the copper the junctions were between the copper itself and No. 30 constantan wire inserted in very small holes in he copper and fastened with a solder of pure silver. For the purpose of checking the behavior of the apparatus, some specimens were equipped with three junctions about equally spaced, and with each of these it was found that the wave velocity between the first and second junctions was the same as that between the second and third.

The device found most convenient for holding the specimen and heating coil *h* is shown in Fig. 2. It consists of three circular disks of asbestos board fastened to a $\frac{1}{4}$-inch iron rod. The two end disks, in order to be readily removable, are clamped by nuts, and the middle one is cemented in place. The specimen is inserted in a hole just large enough to receive it in the central disk, and the opposite end is steadied by means of a bit of wire which ties it to the iron rod. The junction wires pass out through small holes in the right-hand disk. During use the whole arrangement is placed in a small wooden box, or wrapped with a sheet of paper, or inserted in an electric furnace in the cavity of which it just fits.

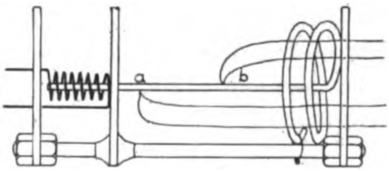

Fig. 2.

The Heating Coil h.—This coil, which is wound from No. 20 nichrome wire, has a diameter of 1 cm. and length of 2.5 cm. Its resistance at room temperature is 1.5 ohms. In the writer's work the maximum current in *h* has been in the neighborhood of 2.5 amperes.

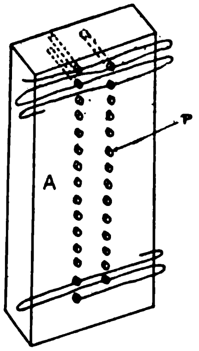

Fig. 3.

The Variable Resistance r.—This resistance is built up in fifty-two equal sections from No. 18 manganin wire, the manner of construction being shown in Fig. 3. *A* is a fiber block through which two columns of copper pins *P* are driven, and the wire, being arranged in a zig-zag form, is soldered to the ends of these pins which project from one face of *A*. The sliding contact which the cam actuates presses against the other ends of the pins. As a result of using a variable resistance of this kind, the current through the coil *h*, instead of varying continuously in agreement with the equation

$$I = I_0 \left| \sin \frac{\omega}{2} t \right| .$$

actually varies by a series of little jumps which approximate closely to the continuous value. However, the result is satisfactory, for with a period as great as eight minutes no lack of smoothness can be detected in the resultant heat-wave in the specimen. The form of this resultant wave has been tested at different times and been found to be strictly sinusoidal.

The Cam.—The cam must be of such a shape as to cause the temperature of *h* to vary in the manner specified by the first boundary condition. Call *c* the heat capacity of *h*, μ its radiation constant, and let $H = H(t)$ represent the rate of development of heat due to a current in *h*. Then the change of temperature of *h* is given by the equation

$$H(t)dt - \mu\theta dt = cd\theta,$$

and since θ must vary according to the relation

$$\theta = \theta_0(\alpha - \cos \omega t), \qquad \alpha \geqq 1,$$

we have

$$\begin{aligned} H(t) &= c\theta_0\omega \sin \omega t + \mu\theta_0(\alpha - \cos \omega t) \\ &= \theta_0[\mu\alpha - A \sin (\omega t + \varphi)], \end{aligned}$$

where

$$A = \sqrt{\mu^2 + c^2\omega^2}$$

and

$$\varphi = \tan^{-1}\left(- \frac{\mu}{c\omega} \right) .$$

Dropping the phase angle φ and remembering that when $I = 0$, $H(t) = 0$, we may write

$$\begin{aligned} H(t) &= A(1 - \cos \omega t) \\ &= 2A \sin^2 \frac{\omega}{2} t, \end{aligned}$$

and since $H(t)$ varies as the square of I,

$$I = \sqrt{2A} \sin \frac{\omega}{2} t,$$

or what, so far as the requirements of the present work are concerned, is equivalent,

$$I = \left| \sqrt{2A} \sin \frac{\omega}{2} t \right| .$$

To get such a current, consider two multiply-connected resistances, h and r, in series with a resistance R and a steady electromotive force. Assume the resistance R to be so large in comparison with h and r that, when h is held fixed and r is varied, the current I_0 supplied by the electromotive force is practically constant. Then, calling I the current through h,

$$I = \frac{I_0 r}{r + h} = a \left| \sin \frac{\omega}{2} t \right|$$

whence

$$r = \frac{ha \left| \sin \frac{\omega}{2} t \right|}{I_0 - a \left| \sin \frac{\omega}{2} t \right|} .$$

Or taking $a = \frac{1}{2} I_0$,

$$r = h \frac{\left| \sin \frac{\omega}{2} t \right|}{2 - \left| \sin \frac{\omega}{2} t \right|} .$$ [1]

Since the value of r is proportional to the displacement of the sliding contact, the radii of the cam (except for an arbitrary additive constant) are given at once by this last expression. The writer has used for the values of ten radii equally spaced in an interval of 180°,

3.75 + 0.000 cm.
3.75 + 0.878 "
3.75 + 1.907 "
3.75 + 3.075 "
3.75 + 4.370 "
3.75 + 5.725 cm.
3.75 + 7.050 "
3.75 + 8.180 "
3.75 + 8.960 "
3.75 + 9.230 "

The cam was run by an electromotor operating through a reduction gearing. The motor was run at as constant a voltage as possible and the change of period of the cam was secured by changing the ratio of the gearing.

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[1] All of this work assumes that the changes of resistance of h and r due to changes of temperature are negligible, and apparently this assumption may be safely made.

The Galvanometers.—These instruments had sensitivities of 118 and 194 megohms, the more sensitive one being connected with the rear junction. They were critically damped, and having equal periods of 3.5 seconds, it was unnecessary to correct for their lag behind the electromotive forces of their respective junctions. They were arranged to cast images of a Nernst filament upon a scale five meters distant.

The time-lag of the rear galvanometer behind the leading one was determined by recording on a chronograph the times of transits of the images of the filament through three reference positions chosen near the center of the swings. The reason for using three positions rather than one will be clear upon referring to the data given upon page 443, for it will be noted that the three values of the time-lag determined during a single complete vibration often vary almost as much from one another as those taken in vibrations several minutes apart. With three reference positions it thus becomes possible to arrive at a given degree of accuracy in about one third the time that would be required when using but one. On the other hand, it was not found desirable to use more than three as the uncertainty incurred by having so many positions to watch counteracted the gain secured by the greater number of readings. The chronograph records were extended to include six to eight vibrations with a period of 130 seconds and from four to six vibrations with a period of 295 seconds. Longer records were not made because slow and irregular changes in the value of μ then had a noticeable tendency to affect the results.

The one condition, which above all others seems to be necessary to an accurate measurement of the time-lag, is that the mean temperature of the junctions remain constant, and until this condition has been attained it is of very little use to take readings.

More sensitive galvanometers than the two the writer has used would doubtless be desirable as it has been found necessary, with the present arrangement, to use a temperature variation at the leading junction of from 20 to 30 degrees Centigrade. Furthermore, with the rear galvanometer considerably more sensitive than the one used, it would be possible, not only to cut down the temperature amplitude, but also to place the junctions farther apart. This would of course increase the time lag and thereby increase the accuracy of the results. With the wires thus far used, damping of the heat wave has been considerable but not so great as was expected. The extent to which this damping occurs does not of course affect the time lag between the galvanometers. Their motions are of the type known as forced vibrations and it can readily be shown that the time lag is therefore determined entirely by their free periods,

Table I.

Tin.

Diam. .25 cm. Length 25 cm. Distance between junctions 2.535 cm. Conductivity .1567.

Period.	Time-lag.			
133.0 secs	7.97	9.04	10.14	
	13.07	11.84	10.82	
	21.04	20.88	20.96	
	9.86	10.90	11.98	
	10.94	9.75	8.68	
	20.80	20.65	20.66	
	10.13	11.23	12.39	
	10.63	9.61	8.42	
	20.73	20.84	20.81	
	9.10	10.30	11.31	
	11.76	10.60	9.56	
	20.86	20.90	20.87	
	9.52	10.54	11.62	
	11.48	10.35	9.26	
	21.00	20.89	20.88	
	9.60	10.79	11.92	
	11.58	10.43	9.33	
	21.18	21.22	21.25	Average = 20.90
297.6 secs.	12.43	13.50	14.37	= 22.64 secs.
	14.08	13.00	11.97	
	26.51	26.50	26.34	
	13.28	14.23	15.19	
	13.34	12.20	11.19	
	26.62	26.43	26.38	
	12.02	13.05	13.94	
	14.53	13.58	12.51	
	26.55	26.63	26.45	
	12.60	13.51	14.48	
	13.89	12.83	11.79	Average = 26.46
	26.49	26.34	26.27	= 28.66 secs.

the degree of their mechanical and electrical damping, and the period of the impressed electromotive force.

III. Data and Results.

Table I. gives a sample set of readings as taken directly from a chronograph record. The three columns give respectively the time-lag (in an arbitrary scale) as determined from the transits occurring at the three reference positions. Motion from the left hand position (corresponding to the left hand column) to the right represents a cooling of the junctions.

Table II. gives in summarized form the results for copper and tin, the two metals upon which thus far accurate measurements have been made.

Table II.

Copper.

Diam. .25 cm. Length 30 cm. Distance between junctions 4.24 cm. Density 8.93.

Date.	Mean Temperature.	Specific Heat.	Period in Seconds.	Time-Lag in Seconds.	Conductivity.[1]	
Mar. 26	35°	.0928	130.7	11.77	...910	.9085 av.
			293.0	15.52		
Apr. 14	35	.0928	129.3	12.12	...907	
			291.3	16.60		
Apr. 16	60	.0938	129.8	12.26	...906	.9035 av.
			293.0	16.97		
Apr. 30	60	.0938	128.8	12.43	...901	
			290.3	17.55		

[1] Unit of conductivity is the calorie per centimeter per second per degree Centigrade.

Tin.

Diam. .25 cm. Length 25 cm. Distance between junctions 2.535 cm. Density 7.28. Mean temperature 35°. Specific Heat .0547.

Date.	Period in Seconds.	Time-Lag in Seconds.	Conductivity.
Apr. 5	129.7	11.30	1551
	290.0	14.36	
Apr. 12	130.1	11.41	1543
	294.5	14.66	
Apr. 12	128.3	11.22	1553
	287.7	14.31	
Apr. 12	133.0	11.32	....1567....1554 av.
	297.6	14.33	

The value of the temperature coefficient for copper as determined (only roughly of course) between the temperatures of 35° and 60° is —.00022, a value which agrees quite satisfactorily with a value found by Jäger and Diesselhorst[1] for one of their specimens of copper. The values of the specific heat of copper which I have used are those of Naccari,[1] and of the specific heat of tin are those of Schimpff.[1] The values of the densities were taken from the *Tabellen* of Landolt and Börnstein.

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[1] Wiss. Abh. d. Phys. Techn. Reichsanstalt, 3, 269, 1900.

Preliminary experiments indicate that the method here described may be advantageously applied to the measurement of the thermal conductivity at high and low temperatures and in a magnetic field, and more extensive measurements are now in progress. Work done with tellurium seems to show that the method will work satisfactorily for conductivities as low as .01.

Cornell University.

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[1] Landolt u. Börnstein, Tabellen.

ON THE CORRECT FORMULA FOR THE DAMPING FACTOR IN HIGHLY DAMPED PERIODIC MOTION OF THE COIL OF THE D'ARSONVAL GALVANOMETER.

BY LINDLEY PYLE.

CONTRIBUTORS to the PHYSICAL REVIEW have discussed the moving-coil ballistic galvanometer in considerable detail from both the theoretical and experimental sides,[1] but a treatment, in this or any other publication, of the narrow limits of applicability of the commonly used formulae for the damping factor has not yet met the attention of the writer. It is becoming the practice to express the damping factor in the form, $(\theta_1/\theta_2)^{1/2}$, instead of in the less simple, but equivalent, logarithmic decrement form, $e^{\lambda/2}$.[2] To show that these expressions are often not even approximations to the truth, and to derive the true damping factor formula, it is necessary to recall certain equations.

The differential equation of motion of a d'Arsonval galvanometer coil is

$$Kd^2\theta/dt^2 + ad\theta/dt + b\theta = 0, \tag{1}$$

where the symbols have the usual significance. It follows that, when the damping is less than critical,

$$\theta = \frac{\omega_0}{s} e^{-\Delta t} \sin st, \tag{2}$$

where ω_0 represents the initial angular velocity when $t = 0$ and $\theta = 0$. $\Delta = a/2K$ and $s = (b/K - a^2/4K^2)^{1/2}$.

Let t_1 represent the time required to reach the first maximum value of θ (see Fig. 1). Then, by eq. (2),

$$2t_1/T = \frac{1}{\pi} \sin^{-1} (1 - a^2/4bK)^{1/2}, \tag{3}$$

where T represents the damped period. $2t_1/T = 1/2$ when $a = 0$, the ratio decreasing in magnitude with increase in a. It will be shown that this ratio is of vital importance in the evaluation of the damping factor,

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[1] O. M. Stewart, PHYS. REV., Vol. 16, p. 158, 1903. Walter P. White, PHYS. REV., Vol. 23, p. 382, 1906. Anthony Zeleny, PHYS. REV., Vol. 23, p. 399, 1906. Paul E. Klopsteg, PHYS. REV., Vol. II., 2d Series, p. 390, 1913 and Vol. III., 2d Series, p. 121, 1914.

[2] Anthony Zeleny, loc. cit., p. 407.

i. e., the factor by which damped galvanometer throws must be multiplied to obtain the values of undamped throws.

If t_1 is the time required to reach the first positive maximum value of θ, say θ_1, then $t_1 + T/2$ is the time required to reach the first negative maximum value of θ, say θ_2 (see Fig. 1). Whence, by eq. (2),

$$\theta_1/\theta_2 = e^{\Delta T/2}. \tag{4}$$

Putting $a = 0$ in eq. (2), the ***undamped*** throw, θ_0, is given by

$$\theta_0 = \omega_0/(b/K)^{1/2}. \tag{5}$$

It can be readily shown that

$$\theta_0 = e^{\Delta t_1}\theta_1. \tag{6}$$

Eliminating Δ between (4) and (6) one obtains

$$\theta_0 = (\theta_1/\theta_2)^{2t_1/T}\theta_1. \tag{7}$$

That is, if damping were to be eliminated, the throw, θ_0, that would

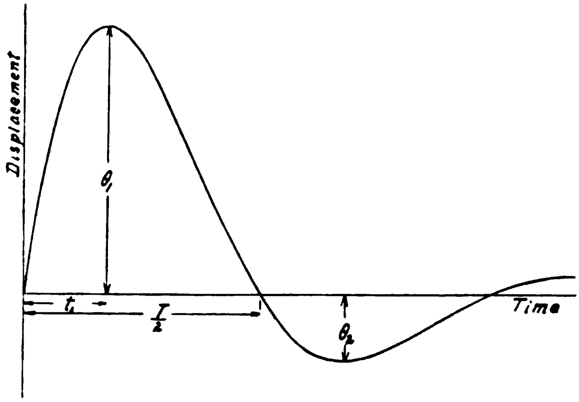

Fig. 1.

then be noted would be $(\theta_1/\theta_2)^{2t_1/T}$ times the observed first throw, θ_1. In short, $(\theta_1/\theta_2)^{2t_1/T}$ is the damping factor. It is customary to write the damping factor as $(\theta_1/\theta_2)^{1/2}$, justifying the expression by citing the constancy of the logarithmic decrement and stating that a ***throw*** corresponds to half (sic) a single swing. The error of approximation in doing this is not negligible unless the damping is small, a fact that has not been adequately pointed out in the literature of the subject. It is therefore of interest to calculate the ratio of the true damping factor to the commonly used damping factor for assigned values of θ_1/θ_2, making use of the following relation,

$$2t_1/T = \frac{1}{\pi}\tan^{-1}\pi/\log_e(\theta_1/\theta_2). \tag{8}$$

θ_1/θ_2 (Assigned).	$2t_1/T$ (Calculated).	$(\theta_1/\theta_2)^{2t_1/T} \div (\theta_1/\theta_2)^{1/2}$ (Calculated).
1	0.5	1
1.2	0.4815	0.9966
1.5	0.4592	0.9836
2	0.4309	0.9532
3	0.3929	0.8890
4	0.3677	0.8325
5	0.3493	0.7846
6	0.3351	0.7442
8	0.3139	0.6791
10	0.2987	0.6291

Fig. 2 shows a plot of columns one and three of the above table. The plotted curve shows at a glance, for any observed ratio of θ_1/θ_2, the true damping factor to be applied to the throw of *any* oscillating system whose motion is correctly defined by eq. (1). Thus, for $\theta_1/\theta_2 = 2.80$, the corresponding damping factor is 0.90 $(\theta_1/\theta_2)^{1/2}$.

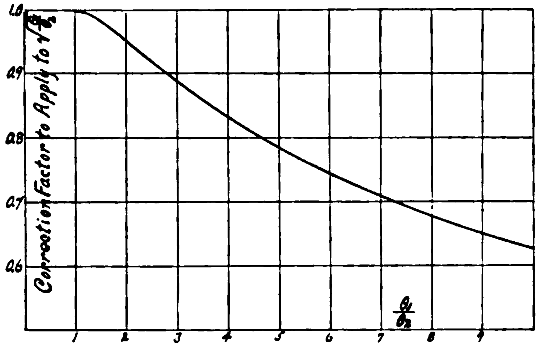

Fig. 2.

The ratio of the damped period, T, to the undamped period, T_0, is given by

$$T/T_0 = (1 + (\log \theta_1/\theta_2)^2/\pi^2)^{1/2}, \tag{9}$$

a formula in which appears the logarithmic decrement but not the damping factor; whence the evaluation of T/T_0 requires no reference to the curve of Fig. 2.

Though it is known that small amplitude oscillations of the suspended system in the moving-coil type of ballistic galvanometer follow very closely the type of motion indicated by (1),[1] it seems worth while to contribute the following comparison of observed and calculated data for the case of a Leeds & Northrup Type HB ballistic d'Arsonval galvanometer. Photographic records were obtained by reflecting a beam of light from the mirror of the oscillating coil to a drum whose periphery, situated 50 centimeters from the mirror, was driven at a constant speed of approximately 7 millimeters per second. The coil was in a closed circuit of total resistance as indicated in the following table, and oscillations were set up by a loose-coupled inductive action of a neighboring circuit. Damping was varied by changing the resistance of the coil circuit. Fig. 1 is a fairly accurate copy, to actual scale, of one of the oscillograms obtained. See also a paper by B. Osgood Peirce.[1] The differences between the observed and calculated values of $2t_1/T$ are no greater than the observational errors associated with the reading of the oscillograms. Furthermore, $(1/T)$ log (θ_1/θ_2) plotted with $1/R$ yields a straight line, as would be expected from consideration of eq. (4) and the fact that that part of a due to the counter electromotive induced in the turns of the coil by its motion is proportional to the conductivity, $1/R$, of the closed circuit.

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[1] B. Osgood Peirce, Proc. Am. Acad., Vol. XLIV., p. 302, 1909.

Circuit Resistance Ohms.	θ_1/θ_2 (Observed).	$T/2$ Sec.	t_1 Sec.	$2t_1/T$.	
				Observed.	Calculated.
20,000	1.556	6.23	2.90	0.466	0.456
7,000	2.083	6.31	2.79	0.442	0.452
5,000	2.554	6.45	2.68	0.416	0.408
4,000	3.017	6.49	2.60	0.400	0.393
3,000	4.145	6.76	2.47	0.366	0.366
2,000	9.072	7.53	2.32	0.308	0.305

The curve of Fig. 2 seems to be of undoubted value in certain experiments involving highly damped oscillations of moving-coil ballistic galvanometers, in that the true corrective factor for damping may be read off without the troublesome, and often difficult, direct determination of the ratio of the time of throw of the coil to its period of oscillation.

Physical Laboratory,
Washington University,
St. Louis, Missouri,
July, 1915.

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[1] B. Osgood Peirce, Proc. Am. Acad., Vol. XLII., p. 166, 1906.

ELECTRICAL OSCILLATIONS FROM MERCURY VAPOR TUBES.

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I. INTRODUCTION.

SEVERAL methods for generating electrical oscillations by means of the mercury vapor arc have been proposed,[1] but the oscillations obtained by these methods are very limited in power or frequency, or are otherwise unsatisfactory. On the other hand, the natural instability and high sparking voltage of the mercury vapor arc would seem to adapt it to the production of powerful high-frequency currents by the Thomson (or Duddell) method. The following research was undertaken to investigate the possibility of obtaining oscillations in this manner. The experimental side of the investigation is confined mainly to mercury vapor tubes, but the theoretical side is generally applicable to arc oscillators in which the amplitude of the high-frequency current exceeds the supply current.

II. PRELIMINARY THEORETICAL CONSIDERATIONS AND EXPERIMENTS.

Arc Oscillations.

As is well known, there are three types of arc oscillations, usually referred to as first, second, and third kinds respectively. Nasmyth[2] has proposed the names "Duddell," "Poulsen," and "Wien" oscillations, which will be adopted here. In Duddell oscillations, the condenser current is smaller in amplitude than the direct current supplied; hence the total arc current is always greater than zero. Poulsen and Wien oscillations consist of condenser discharges of relatively large amplitude, alternating with periods of extinction of the arc. In Poulsen oscillations the condenser discharges are single unidirectional pulses, whereas in Wien oscillations the discharges are of the usual damped oscillatory form. Only the last two types of oscillations will be considered in this paper.

The voltage fluctuations across an oscillating arc give rise to periodic variations in the supply current. In practice, these variations are small, because a large series inductance is always inserted, hence the tendency has been to regard the supply current as constant. It will be shown later that these variations, however small, are of fundamental importance. A description of the cycle of events in arc oscillators, with emphasis on the pulsations in the supply current, is therefore in place.

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[1] See, for example, Vreeland, PHYS. REV., 27, p. 286, Oct., 1908, and U. S. Patent Specification No. 1,079,250 (Lyle).

[2] PHYS. REV., Vol. 32, p. 69, Jan., 1911.

A typical diagram of connections is shown in Fig. 1. E is the source of direct current, R_1R_2 are series resistances, L_1L_2 series inductances,

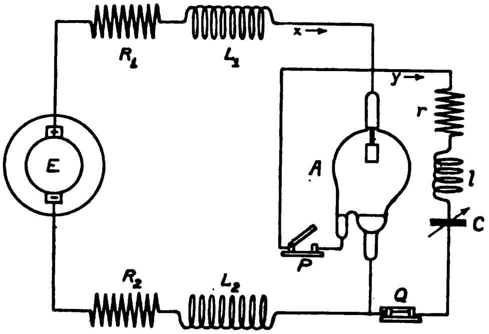

Fig. 1.

and A is any suitable arc, such as a Poulsen or Lepel arc. Condenser C, inductance l and resistance r comprise the oscillatory circuit, which is controlled by the switch Q.

Suppose that switch Q is open and that the direct current is flowing steadily through the arc. Upon closing Q the arc is extinguished, and the inductances L_1L_2 being to discharge their stored energy into the condenser; *i. e.*, the supply current decreases and the condenser voltage increases. This continues till C attains the sparking voltage, whereupon the arc becomes conductive, and allows the impressed E.M.F. to increase the supply current toward its original value. If the oscillations are of the Poulsen type, the arc remains conductive only long enough for the condenser circuit to execute one half swing, at the end of which the arc is again extinguished and the condenser is charged to a negative voltage smaller than the sparking potential. The energy left in the condenser is now returned to the supply circuit, and the supply current therefore continues to increase, till the condenser voltage is reduced to zero. This completes the Poulsen cycle, for energy now flows from the series inductances into the condenser until the sparking potential is reached again, etc. Hence, this cycle may be divided into three periods: (1) arc extinguished, condenser voltage increasing from zero to positive maximum, supply current decreasing; (2) arc conductive, condenser discharging, supply current increasing due to action of impressed E.M.F.; (3) arc extinguished, condenser voltage increasing from negative maximum to zero, supply current increasing due to action of impressed E.M.F. and reversed condenser E.M.F.

In oscillations of the Wien type, as in the preceding case, the extinction of the arc is followed by a decrease in the supply current and a rise of the condenser voltage to the sparking potential; but the ensuing discharge is now of the usual damped oscillatory form. During the discharge, the arc is conductive and therefore allows the impressed E.M.F. to increase the supply current toward its original value. When the energy initially given to the condenser is practically all dissipated or radiated, the discharge ceases and the arc becomes non-conductive again. The condenser then receives energy from the series inductances till the sparking potential is reached, as before, and the cycle repeats itself. Hence this cycle may be divided into two stages: (1) arc extinguished, condenser voltage rising, supply current decreasing; (2) arc conductive, condenser discharging, supply current increasing due to action of impressed E.M.F.

It is readily seen that in both types of oscillations the decreases in the supply current must be greater than the increases during the first cycles, and therefore that the supply current must suffer a permanent reduction. But if a steady state of oscillation is to be reached, the increases in the supply current must eventually compensate for the decreases. Important consequences will be deduced from this in the mathematical section, but one result, which follows from elementary considerations, may be brought out here, viz., that it is the rate of energy dissipation in the oscillatory circuit, and not the sparking potential, which determines the magnitude of the impressed E.M.F. necessary for operation. For, no matter how high the sparking potential may be, it can always be attained by having a sufficiently large series inductance. On the other hand, the impressed E.M.F. has only a limited time in which to make good the decrease in current occasioned by the energy dissipation in each cycle, hence the greater the dissipation, the greater is the necessary impressed E.M.F. This result cannot be avoided by employing a large series inductance, for that affects the increases and decreases equally.

The fluctuations in the supply current have an important bearing also on the design of the series inductance. The functions of this inductance are to conduct the direct current to the arc, to charge the condenser to the sparking potential after each extinction of the arc, and to reflect the high-frequency energy produced so as to localize it in the oscillatory circuits. It is not generally appreciated that the last two functions are of an essentially high-frequency character, and therefore will not be performed to the best advantage if the coils have much distributed capacity. For example, the time of propagation through the series inductance increases as the capacity of the windings is increased; but unless this time is short compared with the time required to raise the condenser to the sparking potential, only part of the coils will be useful in charging the condenser. Other disadvantages result from distributed capacity in the series inductance, which will be dealt with more fully after the mathematical developments have been presented.

Preliminary Experiments.

The foregoing considerations indicate that the successful utilization of the mercury vapor arc in a Thomson (or Duddell) circuit might possibly resolve itself into a question of merely putting a sufficiently large, properly constructed inductance in series with the tube. To test this possibility, a preliminary set of experiments was carried out.

The diagram of connections is that shown in Fig. 1. The condenser C in the oscillatory circuit was varied from 2×10^{-8} to 2×10^{-10} farads, approximately, the inductance l from the lowest values (inductance of the leads) up to about 0.006 henry. The switch P was used in starting the tube by tilting so as to make contact between the starting anode and the cathode in the usual manner. At times the starting anode was used as an operating anode, either alone or in conjunction with the regular anode. The supply voltage E was 240 in the first tests, but later this was raised to 500 and then to 750 volts. The supply current ranged from about 0.5 to about 2.5 amperes, but in most of the tests it was in the neighborhood of 1 ampere. The total value of the series inductance was approximately five henries. This was composed of ten coils arranged coaxially so as to get the greatest mutual and hence maximum total inductance. These coils had an inside diameter of 23.5 cm., an average outside diameter of 32 cm., and an average width of 5 cm. Some of the coils had 30 turns per layer, others had 45. Their D.C. resistances ranged from 6.6 to 40.0 ohms; their low frequency inductances from 0.124 to 0.778 henry. The wire in these coils was insulated with a double cotton covering. There was no extra insulation between layers. The coils having the least number of turns per layer were placed nearest the tube. All apparatus subjected to high voltage was carefully insulated.

The tubes experimented with varied from a small mercury quartz lamp to a rectifier bulb 25 cm. in diameter. In some of the tests the bulbs were cooled by immersing them in oil; in others they were warmed by first passing large currents through them; in others still, no attempts were made to control the temperature.

All efforts to generate steady oscillations in these experiments failed. Irregular pulsations of considerable amplitude, however, were readily obtained, as was shown by a hot-wire ammeter in the condenser circuit. When the system was oscillating in this irregular manner, sparking could be observed between the layers in the coils nearest the tube, but not in those more remote. This gave evidence not only of considerable energy dissipation in the coils, but also that the series inductance was not acting as a unit. It was concluded, therefore, that although the number of turns per layer was not very large, the coils used were not suitable for the purpose. Indeed, subsequent measurements showed that at a frequency of 13,000 cycles the effective inductance of the individual coils was doubled and the effective resistance increased five hundred fold, thus proving that the distributed capacity of the windings is a factor of the greatest importance in such inductances.

It did not seem probable, however, that the series inductances or the rate of energy dissipation alone could be responsible for the negative results obtained. A mathematical investigation was therefore undertaken.

III. MATHEMATICAL DEVELOPMENT.

Assumptions, Notation, Etc.

In the oscillations under consideration, the transitions between conducting and non-conducting states of the arc, though rapid, occupy an appreciable time. Furthermore, when the arc is in the conducting state, its resistance varies with the current. These facts introduce mathematical difficulties, to avoid which we shall assume that the transitions between non-conducting and conducting states are instantaneous, and that the arc resistance, when finite, is constant. These assumptions, which are very similar to those adopted by Maisel[1] in his theory of the "Singing Arc," are certainly as justifiable as the corresponding assumptions usually made to avoid magnetic hysterisis and variable permeability.

The effect of these assumptions on the arc characteristic is indicated in Fig. 2. Here AB is a typical falling "static" characteristic, showing the relation between arc current and voltage when the current is slowly varied. DEC is a "dynamic" characteristic, showing the relation between arc current and voltage when the current is undergoing rapid cyclic variations. Under the above assumptions, the dynamic characteristic becomes the curve composed of the straight line OF and the voltage axis. These curves refer to Poulsen oscillations.

The oscillatory circuit of Fig. 1 is usually coupled with a secondary (antenna) circuit, but from the present point of view, the effect of this is mainly to modify the constants r and l of the primary oscillatory circuit. Hence, it is sufficient to confine the discussion to a system consisting of a supply circuit, an arc, and a single oscillatory circuit only (Fig. 1).

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[1] Phys. Zeit., 6, p. 38, 1905.

In practical cases, the amplitude of the oscillatory current is much larger than the supply current, and this will be assumed in the following. This assumption, while not necessary, simplifies the analysis by enabling an approximate value for the period of arc conduction to be readily found.

Although the periodic variations in the supply current are of fundamental importance, the mathematics is much simplified if these variations are kept small, as they generally are, by the use of a large series inductance. We shall assume, therefore, that the series inductance is large.

The following notation is used:

L = Total inductance of the supply circuit.
R = Total resistance of the supply circuit.
E = The impressed E.M.F. (assumed constant).
x = The Instantaneous value of the current in the supply circuit.
x_m = The mean value of the current in the supply circuit.
l = The inductance of the oscillatory circuit.
r = The resistance of the oscillatory circuit.
C = The capacity of the oscillatory circuit.
y = The instantaneous value of the current in the oscillatory circuit.
v = The instantaneous value of the condenser E.M.F.
q = The instantaneous value of the condenser charge: $q = Cv$.
v_0 = The breakdown voltage or sparking potential of the tube (or other arc).
q_0 = The charge on the condenser corresponding to v_0; $q_0 = Cv_0$.
t_1 = The time during which the tube (or arc) is in a conducting state.
t_0 = The time during which the tube (or arc) is not in a conducting state.
x_1 = The value of x at the end of time t_1.
x_0 = The value of x at the end of time t_0.

Similarly the subsciipts $_1$ and $_0$ will be used to denote the values of other quantities at the end of time t_1 and t_0 respectively. Other symbols will be introduced where necessary. The complete period of a cycle is $t_1 + t_0$, hence the end of time t_0 is the beginning of t_1.

The system is looked upon as in a state of steady oscillation, and the investigation is made to ascertain under what conditions this state is first, a possible one, and second, a stable one.

Fundamental Condition for the Existence of Oscillations.

During the time t_1 the arc is in a conducting state, so that the supply circuit and the oscillatory circuit are both closed through the arc. The two circuits are practically independent of each other during this period, because all they have in common is the arc, and since the resistance of this is small, the coupling effect is small. Neglecting this small coupling, the following differential equations hold:

$$L\frac{dx}{dt} + Rx = E,$$

$$l\frac{d^2q}{dt^2} + r\frac{dq}{dt} + \frac{q}{C} = 0, \tag{1}$$

$$y = \frac{dq}{dt}.$$

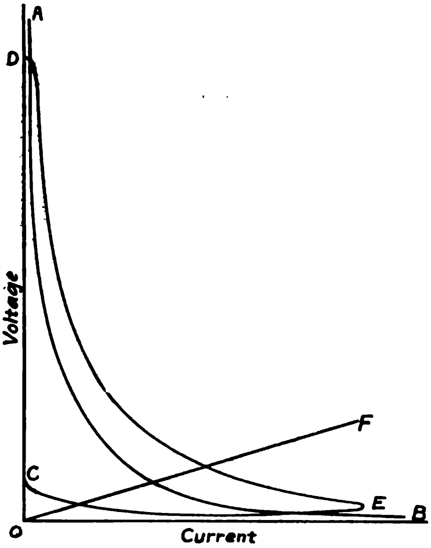

Fig. 2.

At the beginning of time t_1 the condenser voltage has its maximum value v_0, the charge corresponding to this is $q_0 = v_0C$, the oscillatory current is 0, and the supply current has its minimum value x_0. The initial conditions for the equations (1) are therefore:

$$x = x_0, \quad q = q_0, \quad y = 0. \tag{2}$$

Upon integrating equations (1), determining the constants of integration from (2), and neglecting terms multiplied by the small quantity δ_1/p_1, there results:

$$(3)\qquad \begin{aligned} x &= x_0 e^{-\frac{Rt}{L}} + X_0\left(1 - e^{-\frac{Rt}{L}}\right),\\ q &= q_0 e^{-\delta_1 t}\cos p_1 t,\\ y &= -\,p_1 q_0 e^{-\delta_1 t}\sin p_1 t, \end{aligned}$$

where $X_0 = E/R$, $\delta_1 = r/2l$, and $p_1 = \sqrt{(1/lC) - \delta_1^2}$, or $p_1 = 1/\sqrt{lC}$, very nearly. These equations describe the course of events during the time t_1.

The total arc current is $x - y$, and this is 0 whenever the equation

$$(4)\qquad x_0 e^{-\frac{Rt}{L}} + X_0\left(1 - e^{-\frac{Rt}{L}}\right) = -\,p_1 q_0 e^{-\delta_1 t}\sin p_1 t$$

is satisfied. If the oscillatory current is large in comparison with the supply current, as is assumed to be the case here, then (4) is satisfied approximately when

$$(5)\qquad t = \frac{\pi}{p_1},\ \frac{2\pi}{p_1},\ \frac{3\pi}{p_1},\ \cdots$$

After the arc current has passed through 0 for the nth time, the arc remains extinguished and period t_1 is brought to a close. Hence t_1 will be given approximately by

$$(6)\qquad t_1 = \frac{n\pi}{p_1}.$$

If $n = 1$, *i. e.*, if the arc remains extinguished after the arc current passes once through 0, then the oscillations are of the Poulsen type; if $n > 1$, the oscillations are of the Wien type. Mathematically, therefore, Poulsen oscillations are a special case of Wien oscillations.

At the instant $t = t_1$, then, the arc is extinguished, and the second stage of the cycle sets in. In this stage the supply and oscillatory circuits are connected in series so as to form a single circuit with resistance $R' = R + r$, inductance $L' = L + l$, and capacity C. In practical cases, however, r and l are very small compared with R and L; hence the differential equations which hold for the second stage may be written:

$$(7)\qquad L\frac{dx}{dt} + Rx + \int\frac{xdt}{C} = E,$$

or

$$L\frac{d^2q}{dt^2} + R\frac{dq}{dt} + \frac{q}{C} = E,$$

and

$$x = \frac{dq}{dt}.$$

The initial conditions for these differential equations are the final conditions of the first stage of the cycle. Hence the required initial conditions are obtained by substituting t_1 for t in equations (3) as follows:

$$
\begin{aligned}
x &= x_1 = x_0 e^{-\frac{Rt_1}{L}} + X_0\left(1 - e^{-\frac{Rt_1}{L}}\right),\\
q &= q_1 = q_0 e^{-\delta_1 t_1} \cos p_1 t_1,\\
y &= y_1 = x_1, \qquad (8)\\
t_1 &= \frac{n\pi}{p_1} \text{(approximately).}
\end{aligned}
$$

It is to be observed that q_1 may be positive or negative.

Upon integrating (7) and determining the constants of integration from (8), there results:

$$
\begin{aligned}
q &= -(Q - q_1)e^{-\delta_0 t} \cos p_0 t + \frac{1}{p_0}[x_1 - \delta_0(Q - q_1)]e^{-\delta_0 t} \sin p_0 t + Q,\\
x &= x_1 e^{-\delta_0 t} \cos p_0 t + \left\{p_0(Q - q_1) - \frac{\delta_0}{p_0}[x_1 - \delta_0(Q - q_1)]\right\} e^{-\delta_0 t} \sin p_0 t, \qquad (9)
\end{aligned}
$$

where $\delta_0 = R/2L$, $p_0 = \sqrt{(1/LC) - \delta_0^2}$ or $p_0 = 1/\sqrt{LC}$ approximately and $Q = EC$.

These equations represent a free oscillation of the supply and oscillatory circuits acting as one, with the initial conditions $x = x_1$ and $q = q_1$, together with the oscillation due to the presence of the impressed E.M.F., E. They hold from the time the tube is extinguished up to the time when the condenser voltage becomes v_0 and the arc breaks down again. This period, which has been denoted by t_0, is only a small part of a complete cycle of the combined supply and oscillatory circuits, provided that the series inductances are very large. For when this is the case, the voltage range from $\pm v_0 e^{-\delta_1 t_1}$ to $+ v_0$ is small in comparison with the total voltage range (approximately $2x_0\sqrt{L/C}$) of the free oscillation. It follows that $p_0 t$ remains small compared with $\pi/2$, and that $\delta_0 t$ is a small quantity (much smaller than $p_0 t$ in practice). Hence the following approximations are permissible:

$$
\begin{aligned}
e^{-\delta_0 t} &= 1 - \delta_0 t,\\
\sin p_0 t &= p_0 t,\\
\cos p_0 t &= 1 - \tfrac{1}{2} p_0^2 t^2.
\end{aligned}
$$

Upon substituting these values in equations (9) and rearranging, there results:

$$
\begin{aligned}
-q &= \tfrac{1}{2}\delta_0 p_0^2 (Q - q_1) t^3 - \{(\tfrac{1}{2}p_0^2 + \delta_0^2)(Q - q_1) - \delta_0 x_1\} t^2 - x_1 t - q_1,\\
x &= \tfrac{1}{2}\delta_0 p_0^2 x_1 t^3 - \{(\tfrac{1}{2}p_0^2 - \delta_0^2)x_1 + (\delta_0 p_0^2 + \delta_0^3)(Q - q_1)\} t^2 \qquad (10)\\
&\quad + \{(p_0^2 + \delta_0^2)(Q - q_1) - 2\delta_0 x_1\}\, t + x_1.
\end{aligned}
$$

At the end of time t_0, q returns to q_0 as v returns to v_0, and the cycle begins all over again. But a steady state of oscillation can exist only if x returns to x_0 when q returns to q_0, hence it may be stated as the fundamental condition for the existence of oscillations that the two equations

$$\begin{aligned} &\tfrac{1}{2}\delta_0 p_0^2(Q - q_1)t_0^3 - \{(\tfrac{1}{2}p_0^2 + \delta_0^2)(Q - q_1) - \delta_0 x_1\}t_0^2 \\ &\qquad\qquad - x_1 t_0 + q_0 - q_1 = 0, \\ &\tfrac{1}{2}\delta_0 p_0^2 x_1 t_0^3 - \{(\tfrac{1}{2}p_0^2 - \delta_0^2)x_1 + (\delta_0 p_0^2 + \delta_0^3)(Q - q_1)\}t_0^2 \\ &\qquad\qquad + \{(p_0^2 + \delta_0^2)(Q - q_1) - 2\delta_0 x_1\}t_0 + x_1 - x_0 = 0, \end{aligned} \tag{11}$$

shall have a positive real root in common. The equations (11) are obtained from (10) by substituting t_0, q_0, x_0 for t, q, x, respectively, and transposing. The fundamental condition for the existence of oscillations may also be stated as follows: a relation must exist among the coefficients of equations (11) such that the left-hand members shall have a real common factor. This relation can be found rigorously, but the result thus obtained is too complicated for ready physical interpretation. We proceed, therefore, by more approximate methods.

The value of $(x_1 - x_0)$, which occurs in the second of equations (11), may be found from the first of equations (8). The time t_1 is very short, since it is approximately equal to a small multiple of half the period of oscillation of the oscillatory circuit; and since the series inductance is large, the quantity Rt_1/L is small. Hence the approximation

$$e^{-\frac{Rt_1}{L}} = 1 - \frac{Rt_1}{L}$$

may be made with very little error. With this, the first of equations (8) gives:

$$x_1 - x_0 = (X_0 - x_0)\frac{KR}{L}t_0, \tag{12}$$

where $K = t_1/t_0$ is the ratio of time of discharge to time of charge of the condenser.

During the time t_0 the charge on the condenser is changed from q_1 to q_0, hence the supply current must deliver a charge $q_0 - q_1$ during the time t_0. Hence we may write

$$t_0 = \frac{q_0 - q_1}{x_m'}, \tag{13}$$

where x_m' is the mean value of the current during this time. Equation (13) is *a priori* evident, but it may also be regarded as resulting from the solution of the first of equations (11). For, if the latter be solved for t_0, the result is found to be very nearly equal to $(q_0 - q_1)/x_1$, under the assumed conditions. Since equation (13) obviously gives the correct value for t_0, it follows that x_1 and x_m' must be very nearly equal. This proves mathematically that under the assumed conditions the fluctuations in the supply current are small.

Substituting (12) in the second of equations (11), dividing through by t_0, and then substituting (13) in the resulting equation gives:

$$
\begin{aligned}
&\tfrac{1}{2}\delta_0 p_0^2 \frac{x_1}{x_m'}\frac{(q_0-q_1)^2}{x_m'} - (\tfrac{1}{2}p_0^2-\delta_0^2)\frac{x_1}{x_m'}(q_0-q_1) \\
(14)\qquad &-(\delta_0 p_0^2+\delta_0^3)(Q-q_1)\frac{(q_0-q_1)}{x_m'} + (p_0^2+\delta_0^2)(Q-q_1) \\
&-2\delta_0 x_1 + (X_0-x_0)\frac{KR}{L} = 0.
\end{aligned}
$$

We now make use of the fact that the supply current fluctuations are small, hence x_1/x_m' is a quantity very nearly equal to unity. Putting $x_1/x_m' = 1$, $x_1x_m' = x_m^2$, and $x_0x_m' = x_m^2$, where x_m is the mean value of x throughout the complete cycle, there results from (14) after multiplying through by $-x_m$:

$$
\begin{aligned}
&\left(2\delta_0 + \frac{KR}{L}\right)x_m^2 - \Bigg\{(p_0^2+\delta_0^2)(Q-q_1) - (\tfrac{1}{2}p_0^2-\delta_0^2)(q_0-q_1) \\
(15)\qquad &\qquad + \frac{KR}{L}X_0\Bigg\}x_m - \tfrac{1}{2}\delta_0 p_0^2(q_0-q_1)^2 \\
&\qquad + (\delta_0 p_0^2+\delta_0^3)(Q-q_1)(q_0-q_1) = 0.
\end{aligned}
$$

It is to be noted that although the approximations

$$\frac{x_1}{x_m'} = 1, \quad x_1x_m' = x_0x_m' = x_m^2$$

may be made in equation (14) without serious error, this does not mean that $x_1 - x_0$ may be neglected in the second of equations (11), for in the latter $x_1 - x_0$ is a quantity of the same order of magnitude as the other terms.

In practical cases, $R^2C/4L$ is small in comparison with unity, so that in the expressions $(p_0^2 + \delta_0^2)$ and $(\tfrac{1}{2}p_0^2 - \delta_0^2)$, the δ_0^2 may be neglected. Making this approximation, and remembering that $Q = EC$, $q_0 = v_0C$, and $q_1 = v_1C$, equation (15) reduces to:

$$
\begin{aligned}
&R(1+K)x_m^2 - \{E(1+K) - \tfrac{1}{2}(v_0+v_1)\}x_m \\
(16)\qquad &\qquad + \frac{RC}{2L}(v_0-v_1)\{E - \tfrac{1}{2}(v_0+v_1)\} = 0.
\end{aligned}
$$

It can be shown that the last term may be neglected with little error, so that there results finally:

$$E = Rx_m + \frac{v_0 + v_1}{2(1 + K)},$$

$$(17)\qquad \begin{aligned} &\text{where} \quad v_1 = v_0 e^{-\delta_1 t_1} \cos p_1 t_1 = v_0 e^{-n\pi \frac{\delta_1}{p_1}} \cos n\pi_1 \text{ (approximately)} \\ &\text{and} \quad K = \frac{t_1}{t_0} = \frac{n\pi x_m}{v_0 - v_1} \sqrt{\frac{l}{C}} \text{ (approximately).} \end{aligned}$$

Equations (17) exhibit the relation in desired form. They show that due to the presence of steady oscillations, there is a reaction (or counter E.M.F.) in the supply circuit whose average value is given by

$$(18)\qquad P = \frac{v_0 + v_1}{2(1 + K)}.$$

It is this reaction which causes the permanent reduction in the supply current when oscillations are set up, and which is measured by a D.C. voltmeter placed across the arc when it is oscillating. Since the fluctuations in the supply current are small, the product Px_m measures the average power delivered to the oscillatory circuit. As shown by equations (17), the greater the sparking potential, and the greater the damping of the oscillatory circuit (including the arc), and the smaller the ratio of the time of discharge to the time of charge, the greater is the reaction P. It should be noted that this ratio (K) is directly proportional to $\sqrt{l/C}$.

Equations (17) and (18) are general equations holding for all arc oscillations in which the oscillatory current is larger than the supply current. For the special case of Poulsen oscillations we have $n = 1$, in which case (17) and (18) become:

$$(17a)\qquad E = Rx_m + P_2,$$

where

$$(18a)\qquad P_2 = v_0 \frac{1 - e^{-\frac{\pi\delta_1}{p_1}}}{2(1 + K_2)} \quad \text{and} \quad K_2 = \frac{\pi x_m}{v_0\left(1 + e^{-\frac{\pi\delta_1}{p_1}}\right)} \sqrt{\frac{l}{C}}.$$

In Wien oscillations, it usually happens that when the arc is extinguished after the n half-oscillations, the residual voltage v_1 is negligibly small. In this case we have:

$$(17b)\qquad E = Rx_m + P_3,$$

where

$$(18b)\qquad P_3 = \frac{v_0}{2(1 + K_3)} \quad \text{and} \quad K_3 = \frac{n\pi x_m}{v_0} \sqrt{\frac{l}{C}}.$$

The errors involved in the approximations employed in deducing equations (17) and (18) do not exceed a few per cent., provided that the series inductance is very large in comparison with the capacity of the oscillatory circuit. This condition is nearly always fulfilled in practice.

So far as energy relations are concerned, it follows from (17) that steady oscillations are *possible* when

$$E > P.$$

On the other hand, it will presently be shown that in order that the oscillations shall be *stable*, we must have:

$$x_m > \frac{1}{2} \cdot \frac{E}{R}. \tag{19}$$

From (17) and (19) it follows that for stable operation, we must have:

$$E > 2P, \tag{20}$$

i. e.,

$$E > \frac{v_0 + v_1}{1 + K}.$$

For Poulsen oscillations this becomes:

$$E > \frac{v_0}{1 + K_2}\left(1 - e^{-\frac{\pi\delta_1}{p_1}}\right), \tag{20a}$$

and for Wien oscillations:

$$E > \frac{v_0}{1 + K_2}. \tag{20b}$$

Applying these results to the preliminary experiments described above, suppose first that the system tended to produce Poulsen oscillations. The sparking potential v_0 was of the order of 10^4 volts, the factor $e^{-\delta_1 t_1}$ was probably 0.8 or less. The largest value of $\sqrt{l/C}$ was of the order of 10^3, which, with $x_m = 1$ in equation (17*a*) gives a rough value of 1/6 for K_2. Hence P was of the order of a thousand volts, and therefore a supply voltage greater than 2,000 would have been necessary to maintain Poulsen oscillations. If, however, the system tended to produce Wien oscillations (as it probably did), then P comes out somewhat greater than before, assuming that the condenser voltage is reduced to zero in about 10 half-oscillations. It is clear, therefore, that one reason for the negative results in the preliminary experiments is that the supply voltage of 750 was much too low.

STABILITY OF THE OSCILLATIONS AND EFFICIENCY.

We assume, as in the preceding section, that the variations in the supply current are kept small by the use of a large series inductance. The results to be obtained here are otherwise independent of the previous assumptions. One new assumption, however, is introduced, viz.,

$$Px_m = \text{constant},$$

where P and x_m have the same significance as before, but are now to be regarded as measured, rather than calculated, values. P and x_m are the ordinates and abscissæ of the arc characteristic "with oscillations," and experiment[1] shows that such characteristics have much the same shape as the ordinary "static" characteristic, *i. e.*, are approximately equilateral hyperbolas. As a result of experiment, therefore, we are justified in writing

$$\frac{d}{dx_m}(Px_m) = 0 \tag{21}$$

for at least small variations in x_m.

The average rate at which energy is supplied to the system is Ex_m; the average power dissipated in heat in the supply circuit is Rx_m^2, since the fluctuations in the supply current are small. Hence, denoting by U the average useful power delivered to the system, we have

$$U = Ex_m - Rx_m^2. \tag{22}$$

U represents useful power in the sense that it is power supplied to the oscillatory circuit. But the power drawn by the oscillatory circuit is Px_m, since the variations in x are small. Hence

$$Px_m = U. \tag{23}$$

This equation, which expresses the equilibrium between power supplied to and power drawn by the oscillatory circuit, can be true on the average only, owing to inevitable disturbances. If, in a departure from this equilibrium condition, x_m is decreased, and if U is thereby made larger than Px_m, then the oscillations are stable; but if U is thereby made smaller than Px_m, the oscillations are unstable. Hence the fundamental condition for stability is:

$$-\frac{\partial U}{\partial x_m} > -\frac{\partial}{\partial x_m}(Px_m). \tag{24}$$

Using (21), this becomes

$$\frac{\partial U}{\partial x_m} < 0. \tag{25}$$

From (22), U is a maximum when

$$\frac{d}{dx_m}(Ex_m - Rx_m^2) = 0,$$

i. e., when

$$x_m = \frac{1}{2}\frac{E}{R} = \bar{x}_m. \tag{26}$$

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[1] See Nasmyth, loc. cit.

When $x_m < \bar{x}_m$, $\partial U/\partial x_m$ is positive, and when $x_m > \bar{x}_m$, $\partial U/\partial x_m$ is negative. From (25) it follows that the oscillations will be stable only when $x_m > \bar{x}_m$, *i. e.*, when

$$x_m > \frac{1}{2}\frac{E}{R}, \tag{19}$$

which is the relation used in the preceding section to find the impressed E.M.F. necessary for operation.

The condition (19) imposes a limitation on the efficiency of arc oscillation generators. For if η denote the efficiency of the supply circuit, then

$$\eta = \frac{P}{E} = \frac{P}{Rx_m + P}, \tag{27}$$

since $E = Rx_m + P$. From (19) and (27) there results

$$\eta < \tfrac{1}{2}. \tag{28}$$

We have, therefore, the following theorem: In arc oscillation generators supplied with energy from a constant potential source, at least half of the total energy input must be dissipated in heat in the supply circuit.

It should be noted that this theorem refers to the supply circuit only, and says nothing about the efficiency of the arc itself. It should also be noted that the theorem assumes nothing except that Px_m is constant for small variations in x_m and that the pulsations in the supply current are small. Increasing the pulsations in the supply current obviously cannot improve matters, so that the last assumption involves no loss of generality.

The above theorem was first announced by the author in a paper entitled "Preliminary Note on a Mercury Vapor Tube Oscillator," read before the American Physical Society.[1] The detailed proof, however, was not given.

This limitation of the efficiency of arc oscillation generators is serious, but it can be removed (theoretically, at least) by a suitable choice of the source of supply. Suppose, for example, that the impressed force, instead of being constant, falls off linearly with increasing current. Then, writing $(E - hx_m)$ in place of E, equation (22) becomes

$$U = Ex_m - (R + h)x_m^2. \tag{22'}$$

U now has its maximum when

$$x_m = \frac{E}{2(R + h)} = \bar{x}_m, \tag{26'}$$

so that the condition for stability becomes:

$$x_m > \frac{E}{2(R + h)}, \tag{19'}$$

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[1] Phys. Rev., March, 1915, Vol. 5, Second Series.

i. e., the critical current $\bar{x}_m$ is shifted to lower values. Since we now have

$$E - hx_m = Rx_m + P, \tag{17'}$$

the expression for the efficiency is

$$\eta = \frac{P}{E - hx_m} = \frac{P}{Rx_m + P}, \tag{27'}$$

which is the same as (27). From (19′) and (17′) it is clear that Rx_m can be made small in comparison with P by making h large in comparison with R. By this means the efficiency of the supply circuit can be made high. All that is necessary is a source in which the E.M.F. falls off very rapidly with increase of current, *i. e.*, a source which approaches the characteristics of a constant current supply, rather than a constant potential supply. But there is a practical difficulty in the way, viz., the voltage changes must follow the current changes almost instantaneously. For if the arc current goes below the critical value $\bar{x}_m$, a very short time is sufficient for extinction. Thus, for example, if a high-voltage, differentially compounded D.C. generator were employed, the magnetic changes following the current changes in the series field would be much too slow, ordinarily, to be very useful here.

Although the mathematical developments contained herein are original with the author, so far as he knows, the suggestion of using a source whose E.M.F. decreases with increase of current is not new. Chaffee,[1] in giving the efficiency of his arc, omitted the losses in the series resistances, on the ground that they could be done away with by the use of a proper generator. But no explanation was given, and the practical difficulty emphasized above was not mentioned.

It may be added that any device which shifts the maximum value of U to lower values of the supply current will raise the theoretical efficiency limit; but to be effective, the device must be very rapid in action.

From the point of view of the subsequent experiments with mercury vapor arcs, the most important results of the mathematical development are: (1) The impressed E.M.F. must be large (several thousand volts), on account of the large value of P; (2) the series inductance must be large (several henries) and must be constructed so as to act as a unit for the rapid fluctuations of current and voltage; (3) in the oscillatory circuit, the ratio l/C should be as large as possible.

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[1] Amer. Acad. Proc., 47–9, p. 267, 1911.

IV. SUBSEQUENT EXPERIMENTS WITH MERCURY VAPOR TUBES IN DUDDELL CIRCUITS.

The Series Inductance.

The important part played by distributed capacity in the series inductance was mentioned in an earlier section, but the matter requires further attention. Suppose the turns in the coil to be numbered 1, 2, $\cdots p$, $\cdots q \cdots n$, in the other of winding. The energy stored in the dielectric between any two turns p and q at any instant is $\frac{1}{2}C_{pq}V_{pq}^2$, where C_{pq} is the capacity and V_{pq} is the potential difference between those turns. The total electrostatic energy stored in the coil is therefore $\frac{1}{2}\Sigma C_{pq} \cdot V_{pq}^2$, the summation being extended to include every pair of turns in the coil. If the fall of potential through the windings were uniform, V_{pq} would be directly proportional to $(q - p)$. In general, it is clear that the greater $(q - p)$, the larger is V_{pq}. In a single layer coil, as V_{pq} increases, C_{pq} decreases, so that none of the terms in the summation can become large. In a multiple layer coil, however, pairs of turns for which $(q - p)$ is large are brought close together, with the result that the electrostatic energy stored in the coil can well become as large as, or even much larger than, the energy stored in the condenser in the oscillatory circuit. This has several important disadvantages: first, the time of propagation through the coil is increased, so that only part of the coil is really useful; second, instead of a single oscillatory circuit with one degree of freedom, or a pair of coupled circuits with two degrees of freedom, we have a very complicated system with many degrees of freedom, which materially affects the frequency of the oscillatory circuit (or circuits); third, the "choke-coil" effect is very much reduced by the ease with which high frequency energy is propagated through such coils, whereby the protection to the supply is weakened and energy wasted; fourth, oscillations are set up locally in the coils, which involve an additional waste of energy. This is a very important matter, but a more thorough treatment cannot be given here. It may be pointed out, for example, that as a consequence of these considerations, doubt is thrown on the accuracy of arc frequency determinations in which multiple layer series inductances have been employed.

It may be mentioned in this connection that Wills[1] found that the minimum value to which the current through a mercury vapor tube could be reduced without extinguishing the arc depended not only on the magnitude, but also on the *form* of the inductance in series with the tube. Since the distributed capacity and inductance of the choke coils and of the leads act as an oscillatory circuit shunted across the tube, this observation is evidently in accord with the above discussion.

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[1] PHYS. REV., Aug., 1904.

These considerations show that the series inductance should be made up of single-layer coils; or, if multiple layer coils are used, the separation between the layers should be proportional to the number of turns per layer. To meet these requirements, a large inductance (see Fig. 3) was constructed of fifty single-layer spirals, each consisting of eighty turns of copper ribbon 1.27 × 0.0254 cm. in section, the turns being insulated by jute paper ribbon of the same section. The inside diameter of the spirals was 60.3 cm., the outside diameter 68.7 cm. The coils were tested individually at 300 volts and 500 cycles, and were then arranged in a pile, as shown in Fig. 3, and connected in series. The separation between spirals averaged 0.38 cm., except for the two middle ones, which were separated about 2 cm. The complete inductance had a coefficient (measured at 60 cycles) close to five henries, and a resistance to direct current of 41.3 ohms.

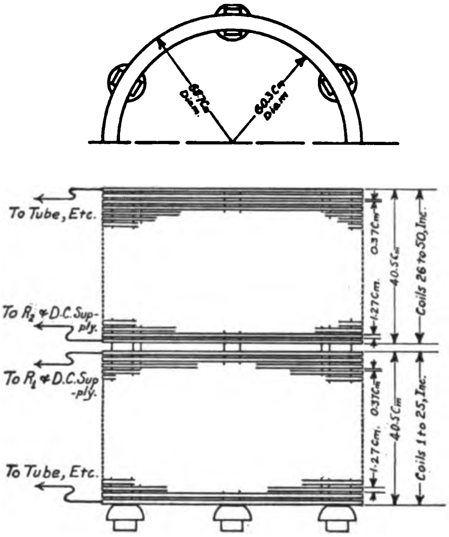

Fig. 3.

A narrower ribbon than 1.27 cm. would have been preferable, but a preliminary calculation showed that the coils ought to be satisfactory for arc frequencies up to 200,000. In order to make sure, however, that the spirals did have too much capacity, one of the coils was subjected to careful wave-meter and bridge measurements. The wave-meter results were 220,000 and 1,400,000 cycles for the natural frequency of the coil alone, and 54,500 cycles for the natural frequency of the coil connected to a condenser of 0.001 mfd. capacity. From these values the equivalent concentrated inductance and capacity of the spiral were calculated to be 0.0080 henries and 0.000065 mfd. respectively, for frequencies not exceeding 220,000. The bridge measurements gave for the effective inductance and resistance of the coil 0.00846 henries and 7 ohms at 13,710 cycles, and 0.00834 henries and 4 ohms at 7,690 cycles. From these results the true inductance was calculated to be 0.00828 henries, which value is probably more correct than the former.

These measurements indicated that the spirals would be satisfactory for a series inductance for arc frequencies up to 100,000 cycles. This was corroborated by the behavior of the inductance in the experiments.

Repetition of First Experiments.

With this new inductance and with an impressed E.M.F. of 4,000 volts obtained from an old motor-generator set, the preliminary experiments described in Section II were repeated. The connections were as before (Fig. 1). The leads from the resistances R_1R_2 (lamps in series-parallel) were connected to terminals of the two middle coils of the inductance, and the tube was connected to the free terminals of the first and last coils. In this way the best voltage distribution throughout the whole inductance and an equal division of the inductance between both sides of this line were obtained.

Variously shaped tubes, different temperatures and different ratios of inductance to capacity were tried, but the results were not much better than before. The most plausible explanation of these negative results seems to be that the damping due to losses in the tube is extremely high. It is quite likely, if the system tended to produce Wien oscillations, as it probably did, that each wave-train lasted only for five or six half-swings, or less. Damping due to spark-gaps or arcs may easily be as large as this; *e. g.*, see Chaffee's[1] oscillograms. Assuming such a short wave-train, the minimum impressed E.M.F. necessary for operation was calculated from equations (17 *b*) and (20 *b*) to be greater than 5,000 volts. The only hope of obtaining oscillations with the available equipment, therefore, lay in decreasing the damping.

The ratio of inductance to capacity in the oscillatory circuit plays a very prominent part in this connection. It controls the damping in accordance with the ordinary laws, and it affects the factor K, as shown by equations (17). But most important of all, perhaps, is its effect on the initial amplitude of the discharge, which, because of the high sparking voltage, tends to very large values. This means that mercury vapor under low pressure, ionized to carry a moderate current, is suddenly called upon to conduct a current many times larger. The principal dissipation of energy in the tube may well lie in the creation of the necessary new ionization at the beginning of each cycle. Increasing the ratio of inductance to capacity is therefore beneficial for three reasons, and special efforts were made to make this ratio sufficiently large. Up to the present time these efforts have not been very successful, but the writer is still of the opinion that steady oscillations can be obtained in this manner. Experiments along the present lines have been discontinued for the time being, because of the discovery of a more promising method.

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[1] Loc. cit.

V. A Double-Cathode Oscillator.

Stability of Parallel Mercury Arcs.

In the course of the preceding experiments attempts were made to lower the damping in the tube by passing two parallel discharges, each from its own cathode to its own anode or to a common anode, simultaneously through the tube. This led to the discovery that two such parallel discharges are much more unstable than a single discharge. Thus, in one instance, when a capacity of 0.002 mfd. was necessary to extinguish the single discharge, a capacity of less than 0.0002 mfd. was sufficient to extinguish one of the parallel discharges. It became evident at once that here was a means of increasing the ratio l/C to a marked extent. An investigation of this matter resulted in the double-cathode oscillator which was briefly described in the paper entitled[1] "Preliminary Note on a Mercury Vapor Tube Oscillator." A more detailed description will now be given here.

Experimental Arrangement and Theoretical Considerations.

The arrangement of the apparatus is shown diagrammatically in Fig. 4. A mercury vapor tube T is provided with two mercury cathodes K_1 and K_2, and an iron or graphite anode A. The cathodes are connected to the negative terminal of the high-voltage generator E through their respective inductances L_1 and L_2 and resistances R_1 and R_2. The anode is connected to the positive terminal of E through the inductance L_3. Between the cathodes is connected the oscillatory circuit consisting of inductance l, condenser C, resistance r, and switch Q.

To facilitate the starting of the discharges, the switch P is provided, which, if thrown to the right, connects cathode K_2 to inductance L_2, and if thrown to the left, connects K_2 to anode A. When the switch is in the latter position, K_2 is an anode; the discharge from cathode K_1 can therefore be started by tilting the tube in the usual manner. After this has been done, the switch P is thrown to the right and the tube is again tilted, which starts the discharge through K_2 without extinguishing that through K_1. During these initial operations, the switch Q controlling the oscillatory circuit should be kept open. If the inductances L_1 and L_2 are sufficiently large, and if they have not too much distributed capacity, the parallel discharges between the two cathodes and the common anode are very stable.

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[1] Loc. cit.

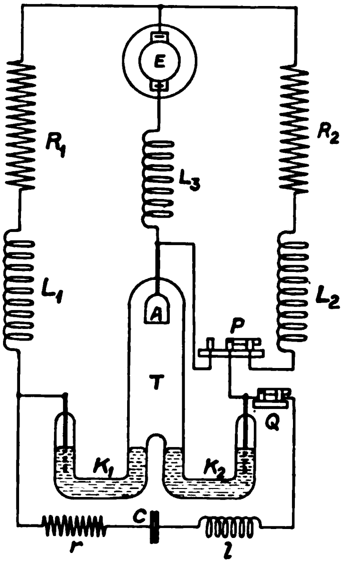

Fig. 4.

When the switch Q is closed, the stability of the parallel discharges is destroyed, and, if the necessary conditions are fulfilled, steady oscillations are obtained. As in the previous case, the oscillations may be divided into two classes, one analogous to Poulsen's, the other to Wien's. The former will be considered first.

Upon closing switch Q, then, the parallel discharges become unstable and one of them, say that through K_2, is extinguished. The current through L_2 must now traverse the oscillatory circuit, and in consequence must decrease while the condenser voltage increases. This continues till the sparking potential is attained, whereupon the vapor between the cathodes breaks down and the circuit Clr begins a damped oscillatory discharge. Simultaneously, K_1 becomes an anode and cathode K_2 becomes operative again. The current through L_2 is now restored to its original path, and therefore begins to increase toward its original value, due to the action of the impressed E.M.F. The current through L_1, on the other hand, must now traverse the oscillatory circuit; hence, while the first half-swing is in progress, there is a small energy transfer between L_1 and C. During the first quarter-period, the direction of this energy flow is from C to L_1, during the second quarter-period from L_1 to C. At the end of the half-swing, the condenser is charged to a reversed voltage smaller than the sparking potential. In oscillations analogous to Poulsen's, which we are now considering, this voltage is insufficient to start the reverse discharge, hence C continues to receive energy from L_1, whose current therefore decreases, till the sparking potential is reached. Thereupon the tube breaks down again, K_2 becomes an anode and K_1 a cathode. The current through L_1 is thereby restored to its original path and therefore begins to increase due to the action of the impressed E.M.F., but the current through L_2 must again traverse the oscillatory circuit. During the first part of the reverse discharge, there is a small energy flow from C to L_2; during the second part, from L_2 to C. At the end of the half-swing the condenser is charged to a voltage smaller than the sparking potential, hence C continues to receive energy from L_2, whose current therefore continues to decrease, till the sparking potential is reached again. The cycle then repeats itself.

We see that in each cycle there is a period of increase in the current through L_1, a period of practically no change, and then a period of decrease. The variations in the current through L_2 are entirely similar. During the first cycles, the decreases in the supply current must be greater than the increases, and the supply current therefore suffers a permanent diminution. But ultimately, equilibrium between the decreases and increases will obtain, when the supply current has been reduced to some mean value x_m greater than the critical value $\bar{x}_m$, provided that the necessary conditions are satisfied. These conditions may be found by a mathematical analysis similar to that which has been given for the previous oscillators. The computation has not been carried out as yet, but it is evident that the results must be of the same general character as those already obtained.

The oscillations described are of nearly pure sine shape; they are therefore analogous to Poulsen's only in that the sparking potential is the same for each half-swing. The sparking potential, however, need not be the same for each half-oscillation, for the first rush of current may ionize the vapor so highly as to permit several successive discharges to pass before the tube regains its sparking potential. We have, therefore, a new kind of oscillations, which are analogous to Wien's. In other respects these oscillations are the same as the preceding, for the extinction of one cathode and the starting of the other at the end of each half-swing must take place as before. The essential difference between the two types of oscillations is, then, that in one the amplitude is constant, whereas in the other it decreases and increases periodically. It should be noted, also, that the frequencies are not exactly the same in both cases.

Kind of Oscillations Generated.

Experimentally, the oscillations generated were always of variable amplitude, and the frequency of the amplitude variations was above audibility. This was determined by coupling the oscillatory circuit very loosely to an Armstrong receiver[1] and observing the character of the sound produced. If the oscillations had been of constant amplitude, a clear note would have been generated in this receiver; actually, however, such a note was obtained but rarely, and then for short intervals of time only. Upon changing the receiver over into the ordinary audion type, the sound produced was a steady hiss, indicating that the frequency of the variations in amplitude was above audibility. This is no proof, of course, that the oscillations generated were of the character described as analogous to Wien's, but the readings of the ammeter in the oscillatory circuit were so steady, and the character of the hiss produced was so regular, that there can be little doubt that the oscillations themselves were very regular. Additional evidence of the regularity of the oscillations is furnished by the occasional production of a fairly clear note in the Armstrong receiver and by the fact that the switch Q (Fig. 4) could be opened so as to draw a high-frequency arc several millimeters long without disturbing the steadiness of the ammeter reading. It seems safe to conclude, therefore, that the oscillations generated were of the character described as analogous to Wien's. The writer hopes that this will receive experimental verification by Braun tube oscillograms.

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[1] U. S. Pat. Spec. No. 1, 113, 149.

Attempts to produce oscillations of constant amplitude were progressing, and it seemed very probable that the desired result would be achieved; but an accident to one of the high voltage generators prevented further efforts along these lines.

Experimental Details.

When the experiments with the double-cathode oscillator were first started, the same difficulties were encountered as in the previous cases. Currents of large amplitude and very high frequencies were easily obtained, but they were almost as irregular as those first obtained. The constants of the oscillatory circuit were varied through a wide range, but it was not until a coil having an inductance of 0.021 henries was inserted in the circuit that very steady oscillations were obtained. Furthermore, it was usually found necessary to warm the tube before attempting to make it oscillate. The range of capacities employed was from 0.002 to 0.0002 mfd. approximately, hence the ratio l/C varied between 10^7 and 10^8; these are extremely high values. But large ratios of l/C cause corresponding reductions in the oscillatory currents, which, in consequence, did not exceed 1.25 amperes (R.M.S. value) in the present experiments. This does not necessarily mean a small available high-frequency current, however, for by closely coupling the oscillatory circuit with another having a much smaller ratio of l/C, the available current can be multiplied many times.

A few additional experimental details are worthy of note. When steady oscillations were first obtained, an impressed E.M.F. of 4,000 volts was used. But even after the accident to one of the generators made it necessary to reduce this voltage to 2,000, steady oscillations could still be obtained, although the adjustments were more critical, of course, and further efforts to obtain oscillations of constant amplitude had to be abandoned. The supply current in these experiments ranged between 0.3 and 0.5 ampere, through each cathode. For resistances R_1R_2 (see Fig. 4), lamps in series parallel were employed. The inductances L_1 and L_2 consisted each of twenty-two of the spirals described in Section IV, the six remaining spirals being used for the inductance L_3. The coefficients were 1.73, 1.71 and 0.21 henry respectively. The use of the six spirals for the inductance L_3 was not resorted to until the generator connected to the anode *A* was injured, repaired, and then injured again so that it could not be repaired. The cause of these disasters was finally traced to the propagation of high-frequency energy through the multiple-layer coil which was then employed for the inductance L_3. There had seemed to be no reason to expect such propagation from the anode, so no special precautions had been taken to protect the generator to which it was connected. When the true state of affairs was realized, the multiple layer coil was replaced by the six spirals referred to, and thereafter no trouble was experienced from that source. This is a striking demonstration of the relative merits of single-layer and multiple-layer coils used as series inductances, choke-coils, etc., in high frequency work.

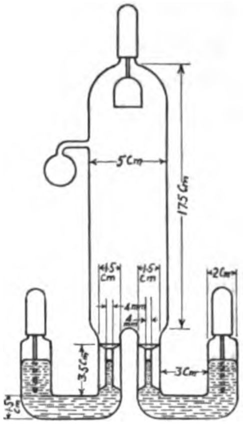

Fig. 5.

In order to determine the most suitable form of tube for the double-cathode oscillator, several different forms were tried. Fig. 5 is a drawing of the tube which gave the most consistent results. It will be seen that the cathodes in this tube are constricted to 4 mm. diameter. This was done, originally, in the effort to lower the sparking potential, but the amount by which the sparking potential was thereby reduced, if at all, was too small to be of much benefit. On the other hand, constricting the cathodes seemed to aid in steadying the action of the tube, although sufficient experiments have not as yet been carried out to ascertain definitely to what extent such constriction is necessary or desirable. Complications in the experiments are introduced by the facts that the temperature of the tube plays a very important part, and that this in turn is affected by the volume of the tube, unless the temperature is controlled by external means.

Frequency Measurements.

It is not the purpose of this paper to enter into the much discussed topic of the frequency of arc oscillations further than to give the results of measurements on the frequency of the present oscillator. These measurements did not go above 80,000 cycles per second, because regular oscillations could not be obtained with an inductance much smaller than 0.020 henry. The lower limit of the measurements was 50,000 cycles, as this was the lowest value for which the wave-meter was calibrated, hence the frequency observations are confined to a rather narrow range. With an inductance of 0.0210 henry, the capacity of the oscillatory circuit was varied and observations were made at arc frequencies of 80,000, 72,800, 65,300, 59,800 and 50,400 cycles per second. The oscillatory circuit was then completely disconnected from the arc, and excited by means of a buzzer. In this way the natural frequencies were determined for the same capacity values as in the preceding measurements, and were then compared directly with the arc frequencies. The results showed that at 80,000 cycles the two frequencies differed by less than the experimental error, that at 50,400 cycles the arc frequency was approximately 2 per cent. lower than the natural frequency, and that between these limits the departure from the natural frequency steadily decreased as the frequency was increased. These departures from the Thomson frequency are relatively very small.

Power and Efficiency.

Owing to its high sparking potential, the mercury vapor tube as an oscillator is best adapted for large powers. But because of the limited output of the high-voltage set, no attempt was made to obtain much power in the present experiments. The resistance of the oscillatory circuit was 33 ohms, so that the actual high-frequency output was 50 or 60 watts. But although its power and efficiency have been very low up to the present time, the general behavior of the oscillator indicates that it is excellently adapted for very large powers.

Comparison with Duddell's Parallel Arc Method.

At first sight it would seem that the double-cathode method described here is but a slight modification of the parallel arc oscillator of Duddell[1] and of Nasmyth.[2] Further considerations show, however, that such is not the case. The most important difference between the two oscillators lies in the fact that in the double cathode method the oscillatory current passes directly between the cathodes, the anode carrying the direct current discharge only, whereas in the parallel arc method the oscillatory current must pass from the cathode to the anode of one arc and thence from the anode to the cathode of the other arc. For this reason the parallel arc method seems to be suitable for Duddell oscillations only, but no such limitation applies to the double cathode method, as has been shown. A further difference, which depends on the character of the arc itself rather than on the system of circuits in which the arc is used, was brought to light by some simple experiments. Three solid carbon rods, arranged as shown in Fig. 6, were connected through large inductances and suitable resistances to the 220-volt supply in such a way as to make one carbon an anode (or a cathode) and the other two cathodes (or anodes). Between the latter a large condenser was connected. By manipulating the carbons, the arcs could be struck so as to start from separate positive craters and remain independent throughout their entire lengths, as shown in Fig. 6, *A*: or they could be struck so as to start from a common positive crater and remain common throughout a considerable part of their lengths, as shown in Fig. 6, *B*. Case *A* is the parallel arc method, case *B* is the double-cathode method. With about 4 amperes flowing through each arc, a capacity of 10 mfd. was always more than sufficient to give violent oscillations in Case *A*, whereas with the same current in case *B*, a capacity of 50 mfd. at times gave no oscillations, at other times only weak ones, depending on the length of arc in common. We see, therefore, that merging two parallel carbon arcs for a considerable part of their lengths markedly decreases the instability, whereas in parallel mercury vapor arcs, the length of positive columns in common has no influence on the instability. This shows that in the carbon arc the seat of the instability is in the ionized column, while in the mercury vapor arc the seat is at or near the cathode bright spot.

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[1] Inst. Electrical Engineers' Journ., 30, Feb., 1901.

[2] PHYS. REV., Vol. 28, p. 459, 1909.

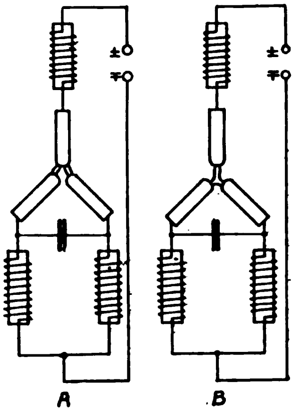

Fig. 6.

Attempts to apply the double-cathode method to other than the mercury vapor and carbon arcs have not as yet been made. Such attempts would be worth while, perhaps, if only for the light which would be thrown on the seat of the instability in the various arcs.

VI. SUMMARY.

A qualitative outline of the theory of arc oscillation generators is given, and the possibility of utilizing the mercury vapor arc in a Duddell or Thomson circuit is discussed. Preliminary experiments with mercury vapor tubes in a Duddell circuit are described, in which a maximum supply voltage of 750 and a series inductance, consisting of a number of multiple-layer air-core coils and amounting to 5 or more henries, were employed. All efforts to obtain steady oscillations failed.

The negative result is partly, but not entirely accounted for by the form of series inductance used. A mathematical investigation is therefore made, the first part of which is based on the assumptions that the transition from the non-conducting to the conducting state of the arc is practically instantaneous, that when in the conducting state the arc obeys Ohm's law, and that the series inductance is very large. The second part is based on the last-named assumption and on the additional one that the product Px_m is constant. The principal results of this mathematical section are:

(1) The average counter E.M.F. P of an oscillating arc is given by

$$P = \frac{1}{2}\frac{v_0 + v_1}{1 + K}.$$

(2) If the impressed E.M.F. is constant, then to insure stability of the oscillations the mean value of the supply current x_m must satisfy the condition

$$x_m > \frac{1}{2} \cdot \frac{E}{R}.$$

(3) If the impressed E.M.F. is constant, then the efficiency cannot exceed 50 per cent.

(4) Stability can be obtained at a lower value of x_m than that given by the above inequality, and the 50 per cent. efficiency limit can be raised, by the use of an impressed E.M.F. which decreases rapidly with increase of current; the voltage changes, however, must follow the current changes almost instantaneously, if the method is to be effective.

(5) To obtain steady oscillations, the supply voltage (if constant) must satisfy the condition

$$E > \frac{v_0 + v_1}{1 + K}.$$

The importance of single-layer coils for the series inductance is discussed. Subsequent experiments with mercury vapor tubes in a Duddell circuit are then described, in which an impressed E.M.F. of 4,000 volts and a series inductance made up of fifty single-layer spirals were employed.

Again all efforts to obtain steady oscillations failed. The negative results can be accounted for by very high damping due to losses in the tube. It is shown that increasing the ratio of inductance to capacity in the oscillatory circuit is beneficial. This ratio, however, could not be increased sufficiently to give steady oscillations with the voltage available.

It is found that two parallel discharges in the same tube, each from its own cathode to a common anode, are much more unstable than a single discharge. The development from this discovery of a double cathode oscillator is described. By preliminary warming of the tube and by increasing the inductance-to-capacity ratio to 10^7, or more, steady oscillations are finally obtained by this method. The frequency of the oscillations did not differ by more than 2 per cent. from the natural frequency of the oscillatory circuit.

The writer wishes to thank Professor M. I. Pupin for his invaluable advice throughout the course of the experiments, and Professor G. B. Pegram for his help and kindly interest. He also wishes to thank Professor Wills for aid in revising the manuscript, Professor Arendt and Mr. Hehre for the loan of lamp-banks, etc., and Mr. Cushman for his assistance in the construction of apparatus. The tubes for these experiments were constructed by the Cooper-Hewitt Company of New Jersey.

Hartley Research Laboratory in Electro-Mechanics,
Columbia University,
April, 1915.

THE EFFECT OF TEMPERATURE ON THE ABSORBED CHARGE AND ON THE CAPACITY[1] OF SOME ELECTRIC CONDENSERS.

By Anthony Zeleny.

A STUDY of the effect of temperature on the absorbed charge in electric condensers may aid in the development of a more complete theory of this charge and lead to a better understanding of what specific factors produce the various observed differences in its magnitude and behavior. The experiments described in this paper were undertaken to obtain some additional data[2] for that purpose. The effect of temperature on the capacity of the condensers under observation was determined at the same time and these results are also given.

The term "*free charge capacity*"[3] will be used to designate the capacity as measured by the free charge augmented by that part of the absorbed charge which passes through the galvanometer during the small fraction of a second it is connected to the condenser. The time allowed for the discharge is not much greater than is necessary to insure the whole measurable part of the free charge to pass through the galvanometer. The term "*true capacity*"[3] will be used to designate the capacity as measured by the free charge alone. Its value is obtained by extrapolation from the "free charge" capacity values at several different known periods of discharge.

A diagrammatic sketch of the apparatus employed for the direct measurement of the absorbed charges is shown in Fig. 1. In the position of the keys shown, the condenser C is charged through a resistance R_1. When the key K_1 is tripped by the pendulum (not shown), the condenser is short-circuited through another resistance, R_2, usually from .01 to .03 second and until the key K_2 is tripped. Then the absorbed charge, as fast as it is liberated, passes through the galvanometer until the circuit is opened at the key K_3. The interval during which the liberated part of the absorbed charge is allowed to flow can be varied by altering the distance between the keys K_2 and K_3. The values of the liberated absorbed charge were calculated from the throws on the assumption that the prolonged flow of the charge produced the same effect as though the whole quantity passed through the galvanometer before the coil moved an appreciable amount.

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[1] A preliminary paper was read at the Washington meeting of the Physical Society, Dec. 27–30, 1911; abstract, Phys. Rev., Vol. 34, p. 141, 1912.

[2] Bibliography of literature on absorbed charges appended to paper by von Schweidler, Ann. der Phys., Vol. 24, p. 766, 1907; Trouton and Russ, Phil. Mag., Vol. 13, p. 578, 1907; Malclès, Journ. de Phys., Vol. 8, p. 631, 1909; Grover, Bul. Bureau of Standards, Vol. 7, p. 495, 1911.

[3] A. Zeleny, Phys. Rev., Vol. 22, p. 65, 1906; A. Zeleny and A. P. Andrews, Phys. Rev., Vol. 27, p. 72, 1908; Curtis, Bul. Bureau of Standards, Vol. 6, p. 431, 1910.

To measure the free charge capacity of the condensers, the electrical connection between the keys K_1 and K_2 in the apparatus of Fig. 1 was removed, so as to avoid the short-circuiting. Then as soon as both of the keys K_1 and K_2 were tripped by the moving pendulum, the condenser began to discharge through the galvanometer and continued until the circuit was opened by the turning of the key K_3. In this manner each condenser was allowed to discharge through the galvanometer for .03 second, except in the case of condenser "*A* 1911" for which the period of discharge was 0.01 second.

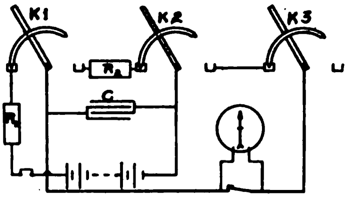

Fig. 1.

Apparatus for measuring the absorbed charge of an electric condenser, liberated in any given time. The keys are operated by means of a moving pendulum which is not shown.

A. CONDENSERS WITHIN METAL CLAMPS.

§ 1. *Absorbed Charge of Paraffin-paper Condenser "A 1911."*

This condenser was made in ten sections, each of which was constructed from two sheets of tinfoil, 6.5 × 32 cm., and two sheets of rice paper 0.06 mm. in thickness. The sheets of rice paper were soaked in warm paraffin and assembled alternating with the sheets of tinfoil. The assembled sheets were then folded, with folds about 5 cm. in length, to form a "rolled" condenser. This, after pressing between flat surfaces, completed the construction which was the same for each of the ten sections. The ten sections were pressed together, connected in parallel, and placed in an iron box, which was then filled with melted paraffin. The cover of the box was at right angles to the plane of the sheets; and therefore the condenser with the paraffin surrounding it may be considered as clamped between metal plates. The determined values of the "free charge" capacity and of the "true" capacity, at different temperatures, are given in Table I.

TABLE I.

Condenser "A 1911."

Temperature.	Free Charge Capacity (.01").	True Capacity.	Difference.
21.°76 C.	.05368 mcf.	.05340 mcf.	.00028 mcf.
8. 65	.05486	.05469	17
0. 00	.05507	.05498	9
− 6. 09	.05524	.05519	5
−19. 5	.05524	.05521	3

The differences in the magnitude of the two kinds of capacity are plotted in Fig. 2. It is believed that this curve gives approximately the amounts of the absorbed charge, per volt, liberated at the different temperatures during the first .01 second of the discharge. The charging electromotive force was 42 volts; the resistance of the galvanometer, 130 ohms; and the period of the galvanometer throw, 3.0 seconds. The resistance of the condenser, measured by the leakage method, varied from 58,000 megohms at 21.°64 to 302,000 megohms at − 19.°5 C.

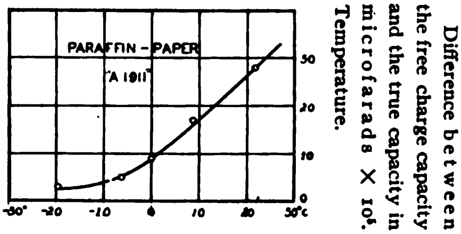

Fig. 2.

The absorbed charge of paraffin-paper condenser "*A* 1911," liberated during the first .01 second including the time during which the free electricity was discharging.

The values of the absorbed charge for various longer periods of discharge from the same condenser were determined by the direct method described above and illustrated in Fig. 1, and are plotted in Fig. 3. The electromotive force of the charging battery was 124 volts, and each of the resistances R_1 and R_2, 130 ohms. The numerals placed beside each curve give, in seconds, the time allowed for the absorbed charge to flow through the galvanometer after the opening of the short-circuit. The absorbed charge liberated during the .01 second that the condenser was short-circuited, did not pass through the galvanometer.

§ 2. *Absorbed Charge of Some Air-mica and of Some Paraffin-paper Condensers.*

This set of condensers consisted of two air-mica and two paraffin-paper condensers, one of each kind having its dielectric untreated, and the other one, having its dielectric baked in an oven for twenty-four hours at a temperature of about 120° C. The tinfoil used was also similarly heated. The mica was assembled with the tinfoil without the use of paraffin, while for the paraffin-paper condensers the paper was dipped into heated paraffin. Each condenser consisted of 5 sheets of tinfoil, 6 × 10 cm., separated by the dielectric, and was clamped between metal plates by brass screws. After the condensers were clamped, the edges were sealed with paraffin to prevent any possible condensation of moisture upon the condenser.

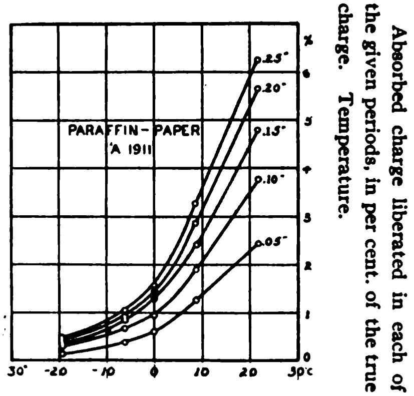

Fig. 3.

The absorbed charge of paraffin-paper condenser "*A* 1911," liberated during the designated periods immediately following the short-circuiting of the condenser for .01 second.

The apparatus of the previous experiment was employed, except that a Leeds and Northrup high sensitivity galvanometer was substituted for the type P instrument. The period of the ballistic throw was 4.5 seconds, and the resistance of the galvanometer coil, 650 ohms.

The condensers, after being charged one minute, were short-circuited for .03 second through a resistance of 1,000 ohms; and the liberated absorbed charge was allowed to flow through the galvanometer during the whole period of its throw. The data concerning the condensers are tabulated in Table II.

The quantities of the absorbed charge, per volt, liberated during the throw of the galvanometer coil are plotted in Fig. 4. They are assumed to be proportional to the voltage.

TABLE II.

Label.	Dielectric.	Treatment of Dielectric.	Charging Voltage.	Remarks.
I	Air-mica	Baked	·78.2	Thickness of mica, .003 mm.
3 II	Air-mica	Untreated	1.4–2.9	Relative humidity of room at time of construction, 72 per cent.
3 VI	Paraffin-paper	Baked	27.7–51	Paraffin boiled in vacuum immediately preceding its use.
33 V	Paraffin-paper	Untreated	4.4–23	Paraffin only just melted.

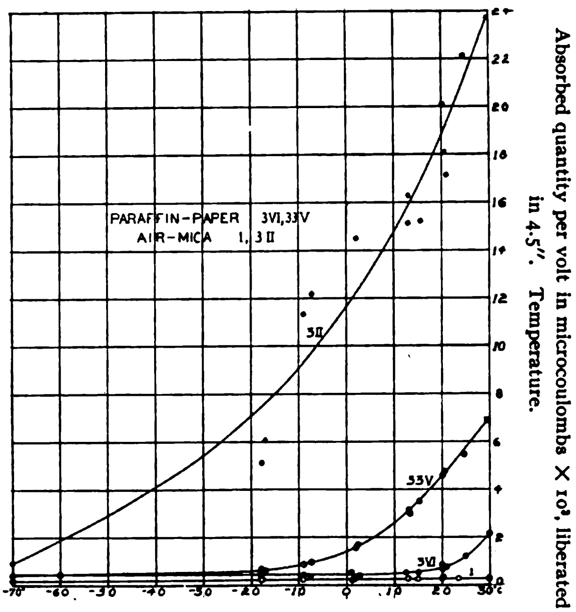

Fig. 4.

The absorbed charge of two air-mica and two paraffin-paper condensers, liberated during the whole period (4.5 seconds) of the ballistic throw immediately following the short-circuiting of the condenser for .03 second.

The same quantities are plotted in Fig. 5, with the ordinates enlarged 10 times.

The same results are again plotted in Fig. 6, but in per cent. of the free charge, the data being taken from the curves of Figs. 4 and 5 and from the corresponding capacities obtained from the curves of Fig. 8.

§ 3. *Capacity of the Clamped Condensers Employed in the Experiments of § 1 and § 2.*

The free charge capacity of the clamped condensers of § 1 and § 2 was determined at the various temperatures employed in the observations

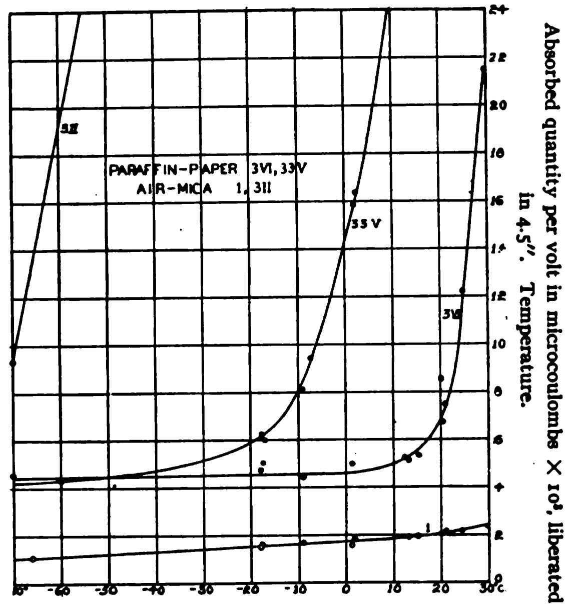

Fig. 5.

The absorbed charge plotted from the same data as the curves of Fig. 4, except that the scale of the ordinates was increased by the factor 10.

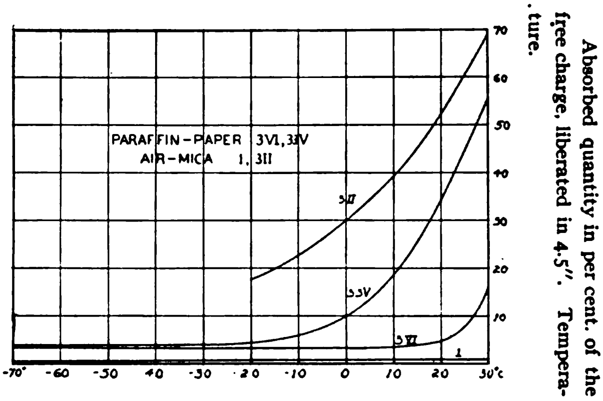

Fig. 6.

The absorbed charge shown in Figs. 4 and 5 plotted in per cent. of the free charge given in Fig. 8.

on the absorbed charge. The results obtained are plotted in Figs. 7 and 8.

The ordinates for condenser "*A* 1911," in Fig. 7, are plotted on a larger scale than those for the other condensers, because there is a greater consistency in the position of the observed points. The observations on this condenser were taken in order from the highest to the lowest temperature; while in the case of the condensers of Fig. 8 some of the observed points were not taken in consecutive order, or were repetitions after observations at other temperatures. Since the irregularity in the position of the plotted points is much greater than the probable observational error, permanent changes in the capacity appear to have taken place with a change in temperature.

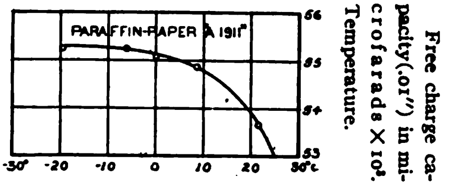

Fig. 7.

The free charge capacity (.01 second) of the clamped paraffin-paper condenser "*A* 1911" whose absorbed charge is plotted in Figs. 2 and 3.

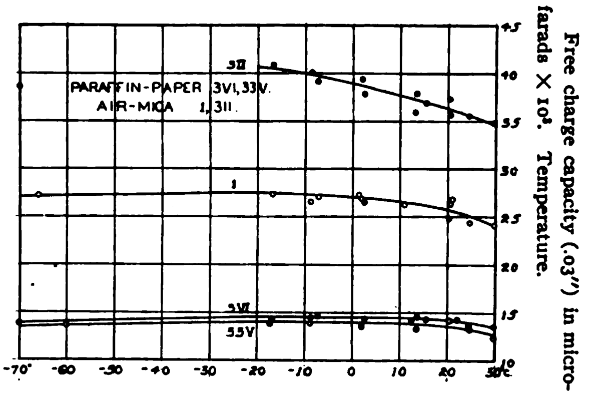

Fig. 8.

The free charge capacity (.03 second) of the two clamped air-mica and the two clamped paraffin-paper condensers whose absorbed charge is plotted in Figs. 4, 5, and 6.

The mean temperature coefficients of the free charge capacity, between 0° and 20° C., for the clamped condensers as obtained from the above curves, are given in Table III.

Table III.

Temperature Coefficients of the Clamped Condensers.

Label.	**Dielectric.**	**Treatment of Dielectric.**	**Change in Capacity per Unit Capacity per Degree, between 0° and 20° C.**
3 VI	Paraffin-paper	Baked	-1.03×10^{-3}
33 V	Paraffin-paper	Untreated	-1.61
"*A* 1911"	Paraffin-paper	Untreated	-1.13
1	Air-mica	Baked	-2.40
3 II	Air-mica	Untreated	-3.33

B. Unclamped Condensers.

§ 4. *Absorbed Charge of Some Paraffin-paper and of Some Ozokerite-paper Condensers.*

This set of condensers was constructed to test especially the effect on the absorbed charge produced by varying amounts of moisture within the same dielectric. The dielectric was rice paper, saturated in a part of the condensers with "paraffin," and in the others, with "ozokerite." All of the condensers were constructed of approximately the same size and in the same manner as one of the sections of condenser "*A* 1911," described in § 1. The condensers, unclamped, were placed into metal boxes which in this case were not filled with paraffin. The boxes, before sealing, contained very dry air, to prevent, later, a precipitation of moisture at low temperatures.

The observations on this set of condensers were taken previous to those of § 2, but in a similar manner; the apparatus being the same with the exception of the galvanometer which was of the same type but having

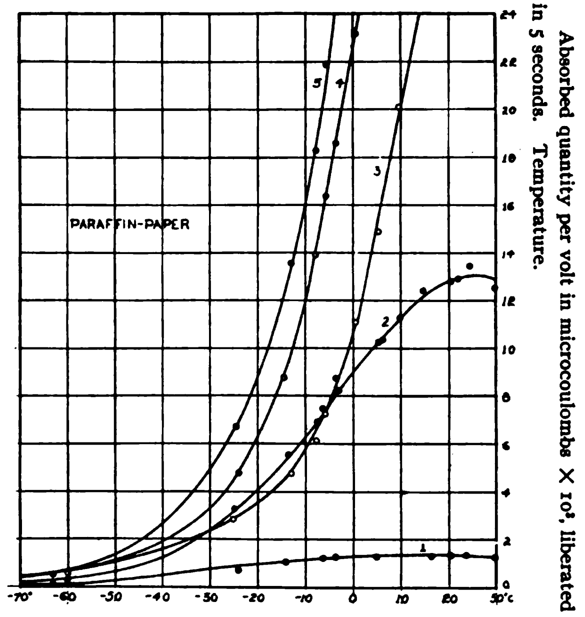

Fig. 9.

The absorbed charge of 5 paraffin-paper condensers containing different amounts of moisture in the dielectric, liberated during the whole period (5 seconds) of the ballistic throw, immediately following the short-circuiting of the condenser for .03 second.

a resistance of 670 ohms and the period of throw, 5 seconds. The condensers are labeled with numerals to indicate increasing amounts of moisture in the dielectric. Through an accident, some doubt is cast on the correctness of this labeling, but it is believed to be correct. The treatment of the paraffin and of the ozokerite in the differently labeled condensers was as follows:

1. Boiling under slightly reduced pressure.
2. Blowing dry air through the melted wax.
3. Untreated.
4. Blowing moist air from the lungs through the melted wax.
5. Forcing steam through the melted wax.

The absorbed charges obtained from the paraffin-paper condensers are plotted in Fig. 9, and those from the ozokerite-paper condensers, in Fig. 10.

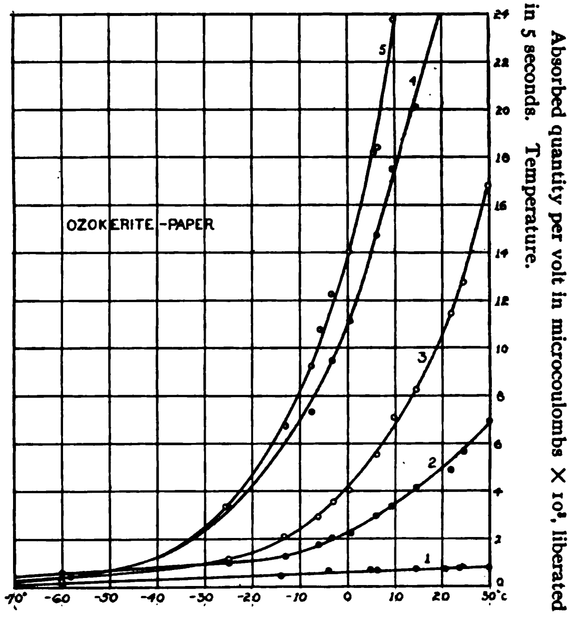

Fig. 10.

The absorbed charge of 5 ozokerite-paper condensers containing different amounts of moisture in the dielectric, liberated during the whole period (5 seconds) of the ballistic throw, immediately following the short-circuiting of the condenser for .03 second.

§ 5. *Capacity of the Unclamped Condensers Employed in the Experiments of § 4.*

The free charge capacities for the paraffin-paper condensers employed in the experiments of § 4, are plotted in Fig. 11, and for the ozokerite-paper condensers, in Fig. 12.

The mean temperature coefficients of the free charge capacity, between 0° and 20° C., for the unclamped condensers as obtained from the curves of Figs. 11 and 12, are given in Table IV.

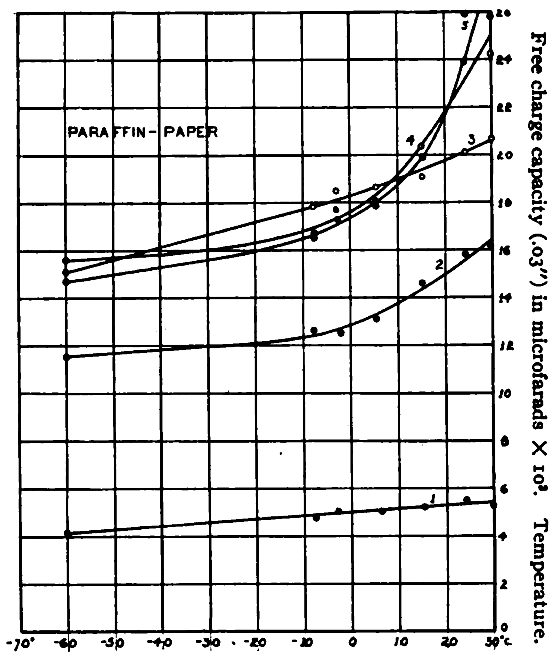

Fig. 11.
The free charge capacity (.03 second) of the 5 unclamped paraffin-paper condensers whose absorbed charge is plotted in Fig. 9.

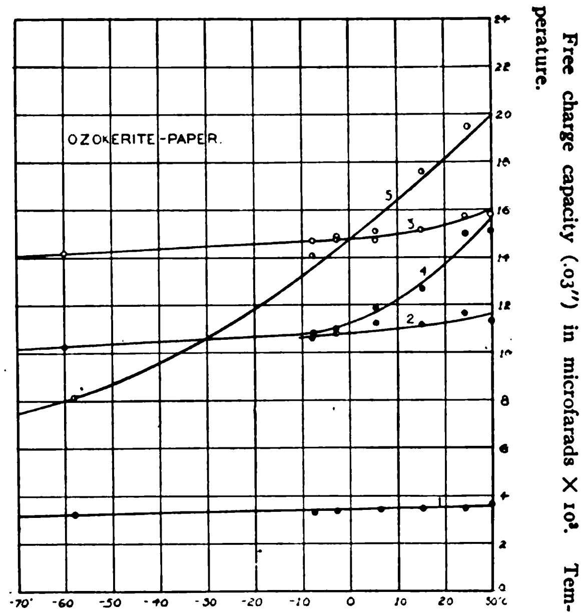

Fig. 12.
The free charge capacity (.03 second) of the 5 unclamped ozokerite-paper condensers whose absorbed charge is plotted in Fig. 10.

TABLE IV.

Temperature Coefficients of the Unclamped Condensers.

Label.	Treatment of Dielectric.	Change in Capacity per Unit Capacity per Degree, Between 0° and 20° C.	
		Paraffin-Paper.	Ozokerite-Paper.
1.	Partial vacuum.........	2.5×10^{-3}	1.5×10^{-3}
2.	Dry air................	8.4	2.0
3.	Untreated..............	4.1	1.9
4.	Moist air..............	11.9	11.0
5.	Steam..................	12.2	11.3

SUMMARY.

The observations given in this paper lead to the following statements in regard to the condensers tested:

1. An increase in the amount of moisture within the dielectric produced a great increase in the magnitude of the absorbed charge at the higher temperatures, and had comparatively little effect at very low temperatures.

2. There is a narrow range of temperature within which, for any particular scale selected for plotting, the absorbed charge curve has a marked change in direction. This has but little more significance than that of indicating where, with the degree of precision employed in the measurement, the change in the magnitude of the liberated absorbed charge becomes considerable. Although the magnitude of the succeeding increments increases with temperature the rate of the increase appears to follow no general law.

3. The greater the amount of moisture in the dielectric, the lower is the temperature at which the absorbed charge, for any particular degree of precision employed, begins to increase rapidly with temperature. This may be explained in the following manner. The greater the amount of moisture in the dielectric, the greater is the number of particles taking part in producing the absorbed charge; and consequently the absorbed charge is greater at any given temperature, and the temperature at which it becomes large enough to have significant magnitude is lower.

4. In those condensers in which the greater part of the absorbed charge is due to moisture, the absorbed charge curve, in general, shows no sudden change in the magnitude of the absorbed charge near the freezing point of water.

5. Clamping of the condensers appears to have no interpretable influence on the absorbed charge.

6. A mica condenser may have a larger absorbed charge than a poor paper condenser.

7. The presence of moisture in the dielectric apparently increases the free charge capacity of a condenser, as well as the magnitude of the absorbed charge.

8. In some of the condensers there is a narrow range of temperature within which the free charge capacity curve, on any chosen scale, has a marked change in direction similar to that of the absorbed charge curve.

9. The capacity curve does not have the portion containing the marked change in direction at the same temperature as the temperature of the similar portion in the absorbed charge curve of the same condensers, when plotted on the same scale.

10. In all the clamped condensers studied, the free charge capacity had a negative temperature coefficient, and in all the unclamped condensers, a positive temperature coefficient. It is of interest to compare this with the observations on commercial condensers taken by Curtis[1] and by Grover.[2]

The graduate school of the University of Minnesota provided assistants from its research fund, who aided in the construction of the condensers and in taking many of the observations.

Physical Laboratory,
University of Minnesota,
July 21, 1915.

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[1] Bul. Bureau of Standards, Vol. 6, p. 447, 1910.

[2] Bul. Bureau of Standards, Vol. 7, p. 495, 1911.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

Minutes of the New York Meeting, October 30, 1915.

THE seventy-ninth meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York, on Saturday, October 30, 1915. Two sessions were held, at 9.30 A.M. and 2 P.M., President Merritt presiding.

The following twenty-eight papers were presented:

A Modified Form of the Moving Lamp Photometer. C. C. Trowbridge and W. B. Truesdell.

Demonstration of a Model Visibly Representing Gas Molecules. E. F. Northrup.

The Fields of Force Surrounding Atoms. Albert C. Crehore.

A New Method of Analyzing the Motion of a Vibrating String. W. S. Franklin.

The Theory of the Flicker Photometer. II. Unsymmetrical Conditions. Herbert E. Ives and E. F. Kingsbury.

The Velocity of Polymorphic Changes Under Pressure. P. W. Bridgman.

Axial Interference Figures from Brookite with Light of Different Wavelengths. John B. Taylor.

A New Line of Argument for the Rigorous Establishment of the Idea of Entropy as a Measurable Quantity. W. S. Franklin and Barry McNutt.

A New Type of String Galvanometer. Horatio B. Williams.

Some Data on the Absorbed Charge in Electric Condensers. Anthony Zeleny.

The Temperature Coefficient of Contact Potential. Karl T. Compton.

Equipartition of Energy and Radiation Theory. (By title.) W. F. G. Swann.

Planck's Radiation Formula Deduced from Hypotheses Suggested by X-ray Phenomena. William Duane.

The Relations of the Photo Potentials Assumed by Different Metals When Stimulated by Light of a Given Frequency. A. E. Hennings and W. H. Kadesch.

Radiation from Tungsten Filaments and the Mechanical Equivalent of Heat. Irving Langmuir.

The Construction of Compound Molecules by Means of the Fields of Force, Especially the Systems of Growth of the Organic Compounds of Hydrogen and Carbon. ALBERT C. CREHORE.

Some New Measurements on the Thermometric Movement of Tree Branches. C. C. TROWBRIDGE.

An Interesting Phenomenon of Wave Motion. W. S. FRANKLIN.

The Value of *h* determined Photoelectrically from the Ordinary Metals. W. H. KADESCH AND A. E. HENNINGS.

Heat Conductivity of Tungsten at High Temperatures and the Wiedemann-Franz Relation. IRVING LANGMUIR.

Atomic Groups in Solids as Indicated by their Thermal Conductivities. ARTHUR H. COMPTON.

A Relation between the Melting Points of Substances and their Heats of Formation. ARTHUR H. COMPTON.

Negative Resistance. ALBERT W. HULL.

Note on an Atomic Model giving a Spectrum Series with Constant Frequency Intervals. ERNEST MERRITT.

The Resistance and Thermo-Electric Power of the Oxides of Iron. C. C. BIDWELL.

A Turbine Type of Molecular Pump. GEO. B. PEGRAM.

Einstein's Photo-electric Equation and Contact E.M.F. R. A. MILLIKAN.

A New Derivation of Planck's Radiation Formula. LEIGH PAGE.

The attendance at each session exceeded one hundred. One hundred and seventeen registered. The next meetings of the Society are at Chicago, November 26 and 27, and at Columbus, December 28–30.

A. D. COLE,
Secretary.

A NEW METHOD OF DETERMINING THE AMPLITUDE OF SOUND WAVES IN AIR.[1]

BY E. P. LEWIS AND L. P. FARRIS.

ESTIMATES of the amplitude of sound vibrations have been made from pressure measurements by Toepler and Boltzmann and Kundt, from energy relations by Rayleigh, and from the vibrations of telephone diaphragms by Shaw. Mach has observed the vibrations of columns of vapor due to sound waves, and Boys set luminous particles ascending from a flame in vibration in the same manner. We have, however, found no discussion of the relations between the amplitudes of vibration of the objects used and those of the sound waves.

It occurred to one of us that the amplitude of the sound waves might be determined from dynamical relations from the observed displacement of illuminated microscopic particles set into forced vibrations by the waves. Preliminary observations showed that suspended particles of ammonium chloride, lycopodium powder, etc., actually participate in the vibrations of the sound waves passing by them. The particles were dropped through a tall chimney-like box of small cross-section with openings on three sides at the same level. Through one a beam of sunlight passed and illuminated the particles. Into the box from the opposite side projected the small end of a funnel, the large end of which was covered with a paper diaphragm. Through the third opening was placed the objective of a microscope which included in its field of view the region adjacent to the open end of the funnel. Near the diaphragm was the open end of an organ pipe of frequency 230. When this sounded the diaphragm was set into vibration, and the sound waves in the funnel, with magnified amplitude at the small end, set the particles in vibration as they fell past the objective of the microscope. Lycopodium powder was the most satisfactory substance tried, as the particles were large enough to fall steadily with no appreciable brownian movement. When the organ pipe was silent the paths of the particles appeared like bright straight streaks against a dark background; when it sounded these lines broke up into well-defined sine curves. Even with a magnifying power of 90 diameters the amplitude of these curves was small, but it is possible to photograph them and to make accurate measurements.

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[1] Abstract of a paper presented at the meeting of the American Physical Society, August 2–7, 1915.

The relation between the amplitude of the particles and that of the sound waves is a simple one. The displacement in the sound wave is

$$x = A \sin \omega t. \tag{1}$$

That of the particle is of the same period but of different amplitude and phase:

$$u = a \sin (\omega t - \varphi). \tag{2}$$

At a given instant the force acting on the particle is proportional to the relative velocity between it and the surrounding medium. If m is the mass of the particle,

$$m\frac{d^2u}{dt^2} = - ma\omega^2 \sin (\omega t - \varphi) = k\left(\frac{dx}{dt} - \frac{du}{dt}\right). \tag{3}$$

Differentiate (1) and (2) with respect to the time, substitute in (3), expand, and equate coefficients of $\sin \omega t$ and $\cos \omega t$. The solution is found to be

$$\tan \varphi = \frac{m\omega}{k}, \tag{4}$$

$$A = \frac{a}{\cos \varphi}. \tag{5}$$

If the particle while vibrating in a horizontal direction falls with a constant velocity v,

$$mg = kv. \tag{6}$$

Eliminating k, (4) becomes

$$\tan \varphi = \frac{\omega v}{g}. \tag{7}$$

A photograph of the sinusoidal curve representing the path of the particle is a chronographic record from which the velocity and the amplitude of the particle may be determined if the frequency of the sound waves and the magnifying power of the system are known, and from these data A may be calculated.

Rough estimates made with a micrometer eyepiece gave the following results, which at least indicate the order of magnitude of the amplitude.

$$n = 230,$$

$$a = 0.0006 \text{ cm.},$$

$$v = 7 \text{ cm./sec.},$$

$$\tan\varphi = 10.35, \quad \varphi = 84^\circ.5,$$

$$A = \frac{a}{\cos\varphi} = 0.0063 \text{ cm.}$$

Further experiments are in progress for the purpose of obtaining quantitative results and determining whether it is legitimate to assume that k is constant for accelerated motion.

Physical Laboratory,
University of California.

A Quantitative Determination of the Earth's Penetrating Radiation.[1]

By Charles Henry Kunsman.

The determination is based upon the assumption that the discharge of an electroscope is due to a leakage across the insulation support and to ionization in the vicinity of the leaf. The source of this radiation is shown to be due principally to the radioactive material in the earth and the atmosphere.

A Spindler and Hoyer aluminum leaf electroscope, with adjustable ionization chambers was employed. By varying the size of the ionization chamber, the ionization effects were separated from the leak across the insulation support. The number of ions formed per c.c. per second, due to the penetrating radiation, may be represented by

$$n = \frac{C_1\delta E_1 - C_2\delta E_2}{(V_1 - V_2) \times e},$$

where C_1 and C_2 are the respective capacities, δE_1 and δE_2 the corresponding drop in potential with the respective volumes of the ionization chambers V_1 and V_2, and e the unit electric charge.

The mean value of n as observed in the basement of South Hall was 8.68, and on the Pacific Ocean from San Francisco to Los Angeles 4.15. A lead screen reduced the ionization on land to about one half its original value. It was also shown that the ionization due to the radioactive material in the atmosphere was not far from .5 ion per c.c. per second. It is interesting to note that the ionization on the ocean and on the land, with the instrument screened, seems to approach a minimum which is about 4 ions.

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[1] Abstract of a paper presented at the meeting of the American Physical Society at San Francisco, August 2-7, 1915.

PHYSICAL LABORATORY,
UNIVERSITY OF CALIFORNIA.

THE ULTRA-VIOLET SPECTRA OF KRYPTON AND XENON.[1]

BY E. P. LEWIS.

THE most complete study of the spectra of these gases has been made by Baly,[2] but his published results do not extend beyond about λ 2415. Photographs of the spectra of the discharge in quartz vacuum tubes furnished by Hilger showed many bright lines extending to about λ 2150, the limit of transmission of the thick quartz system used. The wave-lengths of several hundred new lines have been determined.

Many spectra given by the discharge with condenser and spark gap in the circuit are greatly modified by the addition of self-induction. This is notably true in the case of krypton. A very small inductance will greatly reduce the intensity of the discharge, but by properly increasing the time of exposure it will be found that the intensity of a small number of lines is about the same as in the spectra taken without inductance; a much larger number of strong lines appear to be completely suppressed, while a number of other lines remain, but with greatly reduced intensity.

Baly found that the spectrum of the simple discharge in krypton (the first spectrum) is entirely different from that of the condensed discharge (the second spectrum), and terminated about λ 3500. It is found that the spectrum of the simple discharge extends much further than this, and that, besides the lines of the first spectrum, it includes most of the strong lines which persist with self-induction. This effect is not so pronounced in the case of xenon, although some lines are common to the two spectra. A number of numerical relationships between krypton lines not suppressed by self-induction have been found.

PHYSICAL LABORATORY,
UNIVERSITY OF CALIFORNIA.

TESTS OF THERMO-ELECTRIC FORMULÆ BASED ON BISMUTH AND BISMUTH-TIN ALLOYS.[1]

BY A. E. CASWELL.

THIS paper presents experimental data on the Peltier E.M.F. and thermoelectric power of pure bismuth and of alloys of bismuth and tin containing small percentages of tin.

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[1] Abstract of a paper presented at the meeting of the American Physical Society at San Francisco, August 2–7, 1915.

[2] Phil. Trans., *A* 202, 183, 1903.

It is shown that if the mean free path of the electrons in an alloy is practically the same as in the pure bismuth, and if the electrons which take part in electrical and thermal conductivity are identical with those which take part in thermo-electric phenomena, we have a means of testing the thermo-electric formulae deduced from the electron theory by different authors using different methods.

According to Drude the Peltier E.M.F. should satisfy the equation

$$P = \frac{4\alpha T}{3e} \log \frac{n_1}{n_2},$$

where α is a universal constant, T is the absolute temperature, e is the charge on an electron, and n_1 and n_2 are the numbers of electrons in unit volume of the two metals considered. This formula is equivalent to

$$P = \frac{2RT}{e} \log \frac{n_1}{n_2},$$

where R is the gas constant for a gram-molecule of a gas, and e is the electrochemical equivalent for hydrogen. The latter equation is identical with that deduced by J. J. Thomson and O. W. Richardson if the factor 2 is omitted. The fundamental assumptions in each case have been different. Similarly, in accordance with Lord Kelvin's equation $P = QT$, where Q is the thermoelectric power, we have

$$Q = \frac{2R}{e} \log \frac{n_1}{n_2}.$$

Using the experimental data of Schulze[1] on electrical and thermal conductivities of bismuth and its alloys together with the data given in this paper, it is found that Drude's formulæ are satisfied, but Thomson's are not. The character of the agreement between the data obtained from different sources indicates that the assumptions made in this paper are justified. It is believed that this work definitely links the phenomena of thermo-electricity to those of conductivity in metals.

Per Cent. Tin.	Peltier Effect.	Thermo-electric Power.	Per Cent. Tin.	Electric Conductivity.	Thermal Conductivity.
0	1.000	1.000	0	1.000	1.000
—	—	—	0.34	0.717	0.741
—	—	—	0.71	0.610	0.667
3.75	0.550	0.552	2.15	0.543	0.578
6.36	0.542	0.528	7.43	0.588	0.662
9.93	0.555	0.543	—	—	—

The following table gives the values of the ratio n_1/n_2 computed from various sources, the subscript 1 referring to the alloy and the subscript 2 to pure bismuth. The first and fourth columns give the percentages by weight of tin in the alloy.

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[1] Ann. der Phys., 9, pp. 555–589, 1902.

The work is being continued and its scope extended.

PHYSICAL LABORATORY,
UNIVERSITY OF OREGON.

AN EXPERIMENTAL VERIFICATION OF THE LAW OF VARIATION OF MASS WITH VELOCITY FOR CATHODE RAYS.[1]

BY LLOYD T. JONES.

THE method used in the present verification of the law of variation of mass with velocity is a modification of the usual electrostatic and magnetic deflection photographic method. The method was first used by the writer in a preliminary work for the determination of e/m for cathode rays.[2] With a few minor changes which greatly increased the accuracy of the values obtained it has been applied to the investigation of the variation of the mass of the electron.

The method has the distinct advantage of employing a non-homogeneous cathode beam. The traces on the photographic plate record the paths of electrons of all velocities present. A transformer affording 150,000 volts was used without need of a rectifier or apparatus to produce a uniform discharge potential.

A number of photographs were taken and, due to the great range of velocities present, a verification of the law was obtained from *each* photograph. The results verify the Lorentz-Einstein formula. The range of velocities obtainable with the apparatus was from 5×10^9 cm./sec. to 1.5×10^{10} cm./sec.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
June, 1915.

MAGNETIC FIELDS PRODUCED BY ROTATING SOLID CONDUCTORS IN A MAGNETIC FIELD.[1]

BY S. R. WILLIAMS.

IF a solid aluminum cylinder is rotated in a magnetic field so that the axis of rotation is normal to the field in which it is rotated, a magnetic field is set up normal both to the axis of rotation and to the direction of the applied magnetic field. In this paper a detailed study is made of the magnetic field which is thus established by rotation and some conclusions are drawn as to its bearing upon the problem of magnetization by rotation.

PHYSICAL LABORATORY,
OBERLIN COLLEGE, OBERLIN, OHIO.

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[1] Abstract of a paper presented at the meeting of the American Physical Society at San Francisco, August 2–7, 1915.

[2] Jones, PHYS. REV., N. S., III., p. 317, 1914.

THE HEAT LOSSES FROM INCANDESCENT FILAMENTS IN AIR.[1]

By L. W. Hartman.

FILAMENTS of platinum sponge were mounted in front of an electric furnace, which was subject to temperature control, and heated by means of a current from a storage battery. Through a telescope one could observe these wires against a background of magnesium oxide mounted at the center of the furnace and as they were brought to incandescence a point was finally attained where the wires and the furnace had the same appearance. At this point the wires were assumed to have the same temperature as the interior of the furnace. The power supplied to the wires was then measured and the temperature of the furnace was determined with the Wanner pyrometer. Assuming that these filaments were black bodies and that they radiated energy in accordance with the Stefan-Boltzmann law, the energy loss due to convection and conduction was determined. From these data and observations curves were plotted to show the variation of the energy radiated, the energy supplied, and the energy lost with change of temperature.

In order to separate the conduction and convection losses the effect of introducing the filaments in a vacuum was tried. Curves were then plotted from the data thus obtained, corrected for the absorption of the glass vessel, to show how these losses varied with rise of temperature. This procedure was carried out with both Coblentz's and Gerlach's determination of the radiation constant in order to see which constant, in the light of these data, was the most probable value. As a whole the results seemed to favor the lower value of the radiation constant.

From the tabulated data and the curves it appears that the equation connecting the conduction and convection losses, L, may be expressed thus:

$$L = kT,$$

where T is the absolute temperature and k is a constant for the given wire.

By applying Lorenz's equation to the energy supplied in the case of the first wire one can compute by the method of least squares the two coefficients required in this equation. Adopting Tereschin's assumption that for the different sized wires the radiation coefficient of this equation varies directly with the surface of the wires, the coefficients for the other wires were determined. Computing, with the aid of these coefficients, from Lorenz's equation the energy supplied to each wire, it was found that the observed curves coincide with great exactness with the curves obtained from the computation with Lorenz's equation. It was further found that the curves showing the variation of the energy lost by conduction and convection with temperatures between 900–1700° Absolute coincided more closely with the curve obtained from the equation

$$L = kT$$

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[1] Abstract of a paper read at the meeting of the American Physical Society at San Francisco, August 2–7, 1915.

than from the curve plotted from the values of losses obtained by using Tereschin's method.

UNIVERSITY OF NEVADA.

ULTRA-VIOLET ABSORPTION SPECTRA.[1]

BY R. L. SEBASTIAN.

THE purpose of this investigation was to obtain the ultra-violet absorption spectra of benzene and some of its monosubstitution products, using a new source of illumination. The usual methods of illumination, the cadmium or aluminum spark under water, have always been a source of more or less trouble inasmuch as the water soon becomes turbid and must be changed often. Then, too, the spectra given by these metals are not perfectly continuous.

E. P. Lewis proposed the use of the simple discharge of the hydrogen tube as a source of illumination for absorption spectra in the ultra-violet,[2] which has been shown to give a continuous spectrum in that region. Schniederjost[3] and Frederichs[4] had observed that hydrogen gave a continuous spectrum in the ultra-violet, and the latter used it in trying to obtain ultra-violet absorption spectra using a tube of capillary size which required exposures from twelve to twenty-four hours to obtain a satisfactory plate. By the use of the tube designed by Professor Lewis satisfactory exposures may be obtained in from fifteen to forty-five minutes depending upon the width of the slit and the absorption power of the medium. The tube is a large one, used end on, about thirty centimeters in length and about twelve millimeters in diameter, and has a quartz plate sealed in the end. A pressure of from four to seven millimeters of hydrogen is used. It does not make any material difference if the hydrogen is not completely purified as a little air or water vapor has no noticeable effect upon the spectra, which show perfectly continuous as far as the thick quartz system transmits, *i. e.*, to about λ 2100. The large two-prism quartz spectrograph previously described[5] has a dispersion in the ultra-violet region greater than that given by the first order of a 5-inch grating.

While this work was in progress two articles from Kayser's Laboratory at Bonn have appeared: "Die ultraviolette Absorption einiger Monoderivate des Benzols,"[6] by Christine Strasser; "Zur Strucktur der ultravioletten Absorptionsspektren des Benzols und seiner Monoderivate,"[7] by Rudolph Witte. Both writers have found fairly constant differences between the groups of benzene, and also between the groups of the mono-substitution products, showing that the benzene ring is not changed by the addition of a mono-group.

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[1] Abstract of a paper presented at the meeting of the American Physical Society at San Francisco, August 2–7, 1915.

[2] Science, N. S., Vol. XLI., No. 1069, pp. 947–48, June 25, 1915.

[3] Z. f. wiss. Photo., p. 265, 1904.

[4] Bonn Diss., 1905.

[5] Astrophysical Journal, Vol. 23–5 (June, 1906).

[6] Z. für wiss. Photographie, Photophysik und Photochemie, Vol. XIV., No. 9, pp. 281–311 (1915).

[7] Z. für wiss. Photographie, Photophysik und Photochemie, Vol. XIV., Nos. 11 and 12, pp. 348–391 (1915).

It may be stated, however, that with the better source of illumination and greater dispersion of the spectrograph many new absorption bands have been found which are not mentioned in either of the above papers. It will be interesting to see if the relationships they claim to have found will hold when these new bands are taken into account.

Physical Laboratory,
University of California.

The Oxide Resistance Thermometer.[1]

By S. L. Brown.

The rapid variation of resistance of the metallic oxides with temperature has been utilized to measure temperature. The greatest obstacle in the use of the oxide resistance thermometer is the difficulty in making electrical connections to the oxides. Heretofore connections have been made by clamping wires against the ends of the oxide resistance-element. The author now makes electrical contact by brazing; that is, a small globule of the molten oxide and the molten ends of the wires are brought into contact and allowed to cool.

If good connections are made in this manner, a very satisfactory resistance thermometer can be had which will have a resistance of only 50 to 100 ohms at room temperature, but the resistance will be nearly doubled if its temperature is reduced to ice-point. In many cases, thermometers made in this manner will have many thousand ohms resistance. In all probability, poor connections to the wires accounts for this high resistance. The high resistance thermometers have variable resistances depending on the strength of the current sent through them. Heat produced at poor contact would decrease the resistance and hence the element would have lower resistance for higher currents. Such a high resistance element makes a very satisfactory and sensitive thermometer if used at constant current. Temperatures may be recorded in terms of the resistance which must be added in series with the thermometer in order to keep a constant current, which is furnished by a constant voltage supply. A temperature change of 20 degrees Centigrade may cause a resistance change of 15 or 20 thousand ohms in such a thermometer.

The University of Texas.

A New Form of Radiation Pyrometer.[1]

By S. L. Brown.

The plan in this instrument is to replace the thermo-junction of the Fery radiation pyrometer with an oxide resistance-element. The radiation from the hot body whose temperature is to be measured is focused, by means of a concave mirror, on a very small and thin oxide element. This element is connected in series with a constant voltage battery and a high resistance millivoltmeter. The current, as indicated by the deflection of the millivoltmeter, is a measure of the temperature of the body whose radiation is focused on the high resistance oxide element.

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[1] Abstract of a paper read before the meeting of the American Physicial Society at San Francisco, Aug. 2–7, 1915.

The instrument may be adapted to any temperature interval by shunting the millivoltmeter with the proper resistance. For example, a temperature change from 1600 to 2100 degrees Fahrenheit may cause a deflection of the millivoltmeter from 50 to 125 with a particular shunt while this same district of the millivoltmeter scale may correspond to temperatures below 1600 degrees Fahrenheit when a higher resistance shunt is used.

THE LAW OF COHESION IN MERCURY.[1]

By P. A. Ross.

WHEN a monatomic liquid is warmed the heat is expended in three ways:

1. Increasing the kinetic energy of the molecules.
2. Expanding the liquid against external pressure.
3. Expanding the liquid against internal or cohesion pressure.

If the first is assumed to be equal to the specific heat of the substance as a gas at constant volume the value of the third may be computed since the sum of all three is equal to the specific heat of the liquid.

Using values for the specific heat and density of mercury at 5° intervals from 0° to 360° C. from Landolt-Börnstein Tabellen the relation of cohesion to molecular distance was found to follow very closely an inverse sixth power law.

The force per molecule was then computed and integrated for the removal of a gram of molecules to an infinite distance. This gave for the latent heat of vaporization values ranging from 41.1 calories (Milthaler's data) to 59 calories (Naccari's data) instead of the experimental value of 68 calories per gram.

Leland Stanford Junior University,
July 19, 1915.

THE APPLICATION OF PHYSICAL PRINCIPLES TO PROBLEMS SUGGESTED BY OCEANIC CIRCULATION AND TEMPERATURES.[1]

By George F. McEwen.

MOST of our quantitative knowledge of the great ocean currents depends upon the difference between the true position of a ship and that determined from "dead-reckoning"; and upon observations of floating objects. This work has been supplemented by current meter observations in a few limited regions. Also the distribution of ocean temperatures, which is intimately connected with the motion of the water is an important though indirect source of information concerning ocean currents.

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[1] Abstract of a paper presented at the San Francisco joint meeting of the Physical Society and Section B of the A. A. A. S., August 2–7, 1915.

However the temperature data have been used only in a qualitative way for this purpose. This paper is a summary of some of the quantitative results I have obtained by attempting to calculate the velocities of both horizontal and vertical currents from the distribution of temperatures.

First, assume that the average flow of the water in any direction is negligible, and the depth exceeds 100 meters. Assume the rate of absorption of radiant heat by the water to be an exponential function of the depth, and the rate of loss to be proportional to this exponential function and to a linear function of the temperature. From the observed relation of the mean annual surface temperature and the annual range of the surface temperature to the latitude and also from the assumption that the amount of radiant energy penetrating the water surface is proportional to the solar radiation incident on a horizontal surface at that time and latitude, the normal temperature can be expressed as a function of the depth, latitude and time. The constants for this expression have been determined and the temperatures, computed for various positions, depths and times at which normal values would be expected, agreed well with the observed values.

The influence of a horizontal current was estimated by adding to the differential equation first used a term expressing the rate of gain of heat due to the difference in temperature between the water flowing into an element of volume and that flowing out. By assuming the velocity along stream-lines from various points along the west coast of North America to be proportional to the average wind velocity over them, the temperatures as modified by this surface drift were computed and found to agree well with the observed values. Moreover the relative velocity of the wind and current thus found were in good agreement with those determined in other localities by direct measurement.

The relatively low temperatures of the inshore water along the Pacific coast is regarded by many to be the result of the local up-welling of cold bottom water. Assuming a vertical current with a velocity proportional to that of the wind parallel to the coast as required by Ekman's theory of oceanic circulation serial temperatures corresponding to average monthly values off San Diego were computed and found to agree well with observations. Also some results computed from salinity observations confirmed the above conclusions regarding the circulation.

The author expects to continue the study of this problem and to pubish the methods and results in detail, as soon as possible.

Laboratory of the Scripps Institution for Biological Research.
La Jolla, California.

The Efficiency of Astronomical Spectrographs.[1]

By J. H. Moore.

TWO conditions of fundamental importance control the design of spectrographs for most work in astronomy, which in general do not have to be met in the laboratory. First, celestial light sources are for the most part of feeble intensity; second, in order to avoid loss of light, the spectrograph must be mounted on a moving telescope and hence is subject to the varying component of gravity, as well as to the changing temperature of a well-ventilated dome.

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[1] Abstract of a paper presented at the San Francisco joint meeting of the Physical Society and Section B of the A. A. A. S., August 2–7, 1915.

The losses of light in the various parts of the combined telescope and prism spectrograph are considered and the broad principles indicated in accordance with which the various parts of the instrument must be arranged in order to give maximum light efficiency, when used for the study of the two different classes of celestial objects, stars and extended surfaces.

One of the most important factors in the design of stellar spectrographs which shall give spectra of maximum intensity is shown to be the proper balancing of the two conflicting elements, the transmission at the slit and the transmission of the prism train. A practical illustration is given of the relative efficiency of two spectrographs in actual use at Mount Hamilton in the determination of the radial velocities of gaseous nebulæ,—a one-prism spectrograph, and a three-prism with a camera of 1/3 the focal length of the former. For extended objects the three-prism is about 5 times as fast as the one-prism; for stellar objects, however, its efficiency is only about 50 per cent. greater than that of the one-prism.

The successful design of an astronomical spectrograph, which shall give maximum efficiency in any particular line of research, is a bundle of fortunate compromises between the various conflicting elements of light transmission in the optical system and the construction and arrangement of its component parts so that they shall have the maximum rigidity.

LICK OBSERVATORY,
MT. HAMILTON, CALIF.

ON THE NATURAL CHARGES OF METALS.[1]

BY FERNANDO SANFORD.

THE paper undertakes to show that the phenomena of contact electrification may best be explained on the assumption that different metals (and presumably all other bodies) have definite natural charges of electricity which are capable to inducing charges in other metals when brought near them. The Volta contact charges discovered by Bennett and Cavallo are apparently the bound charges upon the metals due to their mutual induction when they are brought together and their free charges are allowed to escape. The induced free charges were first investigated by Exner and have been discussed by Majorana under the name of approach charges.

Experiments are described by which it is shown that metals while in contact with the earth or with the inside of an earthed hollow conductor may still induce free charges upon other insulated metals near them.

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[1] Abstract of a paper presented at the San Francisco joint meeting of the Physical Society and Section B of the A. A. A., S. August 2–7, 1915.

It is shown that when two metallic bodies are placed within a hollow conductor of another metal their reciprocal induction is modified by the bound charges induced upon both by the surrounding hollow conductor.

It is also shown that a change in temperature of a metal changes the magnitude of its induction upon another metal, and accordingly changes the contact charge between it and the other metal.

It had previously been shown by the writer that the contact electromotive series is the reciprocal of the cohesion series in metals. It is here shown that iron or steel becomes more electronegative with an increase of temperature up to 150 or 200 degrees Centigrade, after which it becomes more electropositive with a rise of temperature. Quotations are given from the writings of other investigators to show that the tensile strength of iron and steel likewise increases with the temperature to about this same point, and that the tensile strength begins to diminish at about the temperature where the temperature coefficient of contact electromotive force changes its sign.

It is suggested that this coincident change of contact electromotive force and cohesion with change of temperature is due to a change in the specific inductive capacity of the metal, and that the Thomson effect in metals may be explained by this change.

Leland Stanford Junior University.

New Units in Aerology.[1]

By Alexander McAdie.

Anemometry is in an unsatisfactory state. There is need of instruments giving a record of the *vertical* flow of the air as well as the *horizontal*; and some indication of *gustiness* or discontinuity of flow. The writer criticizes the wind data of all official weather services as incomplete. In general only horizontal change of flow of air is given and then only for eight points of the compass, one direction covering 45°, entirely too large an angle. Directions should be recorded in degrees beginning with the North and progressing through the West to South, this because the prevailing winds are west and the circulation is contra-clockwise or characteristic of storm circulation in the northern hemisphere.

It will be a great step forward when velocities of flow of air or winds are expressed in absolute force units. To accomplish this, the use of pressure tube instruments is advocated in place of revolving cups, it being also pointed out that the correction factor for the latter is in error more than 20 per cent. and therefore official wind data are practically worthless, although much time is spent in accumulating such data.

The writer strongly urges the use at present of the *meter per second* as a velocity unit and the speedy abandonment of miles per hour or feet per second. Nearly all the nations of the world, the United States excepted, use the m./s.

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[1] Abstract of a paper presented at the San Francisco joint meeting of the Physical Society and Section B of the A. A. A. S., August 2–7, 1915.

Aerostatic pressure, also the vapor pressure, should be expressed in absolute force units, the practical unit being the *kilobar* or 1,000 dynes. The bar thus defined is a strictly C.G.S. unit being the force whlch would impart an acceleration of one centimeter to a gram per second per second. All barometer scales should be regraduated, fractional parts of the inch to be replaced by barokils. Reduction to standard plane of 1,000 kilobars (an absolute atmosphere) can then be accomplished by one operation using some such device as that of Gold of the British Meteor. Office. Fahrenheit and Centigrade temperature scales to be abandoned; and the Absolute Centigrade used, the first of the three figures (generally 2) to be written once in tabular work at head of column. The use of minus signs for low temperatures (such as frequently occur in winter, also in all upper air work) is thus avoided. It is conceded that the scale division, the Centigrade degree, is too large for many purposes. Possibly later, some value 2.73 times as large as this may be agreed upon and this unit divided into tenths.

The water of the atmosphere in solid or liquid form should be expressed not in fractions of an inch but in millimeters. The United States is the only nation of importance that still records rainfall in inches. Eventually depth of water must be expressed in force units.

Blue Hill Observatory,
Harvard University.

Radiation and Atmosphere.[1]

By C. G. Abbot.

A SUMMARY was given of the income and outgo of radiation to and from the earth, its distribution in the spectrum and the effects produced by the various constituents of the atmosphere. Solar radiation ranges principally from 0.3 μ to 3.0 μ, with a spectrum distribution comparable to but differing from that of the perfect radiator at 6500° Abs. C. Terrestrial radiation ranges principally from 5.0 μ to 50. μ, with a spectrum distribution which so far as its source is water (69 per cent.) or vegetation (20 per cent. (?)) is approximately that of the perfect radiator. Naked soil and rock differs from perfect radiator greatly as shown by Coblentz. Mean temperatures on earth's surface range from about 270° to 300° Abs. C. for the various zones of ocean and vegetation. Rock and soil temperatures may run 50° C. higher by day and somewhat lower by night than water and vegetation temperatures. The average spectrum distribution for terrestrial surface radiation is comparable to that of the perfect radiator at 290° Abs. C. Spectrobolometric work, confirmed by self-recording pyrheliometers raised to 25 kilometers altitude by sounding balloons, fix the mean income of radiation from the sum at 1.93 calories per cm.^{2} per min. The solar radiation received varies 7 per cent. per year with solar distance, increases perhaps 3½ per cent. per 100 sun-spot numbers, and fluctuates from day to day irregularly, sometimes through a range of 10 per cent. in 10 days, but usually much less. Solar variation is confirmed by experiments on relative brightness of centre and edges of sun.

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[1] Abstract of a paper presented at the San Francisco joint meeting of the Physical Society and Section B of the A. A. A. S., Aug. 2–7, 1915.

Principal hindrances to direct income of solar rays through the atmosphere are: (1) Clouds; (2) molecular scattering; (3) dust associating itself with water vapor to form haze, or remaining suspended at great elevations after severe volcanic eruptions; (4) selective absorption of water wapor; (5) selective absorption of oxygen; (6) selective absorption of carbon dioxide; (7) selective absorption of ozone. The last three are relatively unimportant. Above 1,700 meters on clear days the losses are almost wholly due to molecular scattering and absorption by water vapor. Fowle computes from observed sky transparency above Mt. Wilson the number of molecules per cm.^{3} at standard conditions as $(2.70 \pm 0.02) \times 10^{19}$. Coefficients of atmospheric transmission for different wave-lengths and figures on the absorption of water vapor at different levels were given.

Principal hindrances to direct outgo of terrestrial rays are: (1) Clouds; (2) water vapor; (3) carbon dioxide; (4) ozone; (5) dust; (6) molecular scattering. Owing to the great wave-lengths concerned, the last two are relatively unimportant. Much investigation is yet required for a satisfactory knowledge of the others. Reference and abstract was given on nocturnal radiation experiments of A. K. Ångström, whose paper is just being published by the Smithsonian Institution.

SOLAR OBSERVATORY OF THE SMITHSONIAN INSTITUTION,
PASADENA, CAL.

SOLAR RADIATION AND TERRESTRIAL MAGNETISM.[1]

BY L. A. BAUER.

DOUBTLESS the chief instruments of research from which we may expect definite knowledge respecting certain salient physical characteristics of the highest levels of the atmosphere, are the self-recording instruments installed at magnetic observatories for the purpose of registering the countless fluctuations to which the earth's sensitive magnetic field is continually subject. The paper shows the rôle which certain terrestrial-magnetic phenomena may play in opening up to us the possible electrical conditions which must obtain in atmospheric regions, 100 kilometers and more above the surface.

Special attention is paid to the conclusions derived from refined magnetic observations made during periods of increased or decreased solar radiation, as, for example, during times of total solar eclipses, or from a concomitant study of variations in the solar constant, as shown by Abbot's observations, and of magnetic fluctuations. It would appear that the Earth's magnetic field undergoes appreciable changes during the time of a total solar eclipse, or during the periods of change in solar radiation shown by Abbot's solar-constant values. As a preliminary conclusion it is found that a ten per cent. increase in the solar constant corresponds to a decrease of about one-fiftieth of a per cent. in the magnetic constant employed as a measure of the variations in the Earth's magnetism.

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[1] Presented at the joint meeting on Atmospheric Physics of Section B, A. A. A. S. and of the American Physical Society, San Francisco, Aug. 1915.

The bearing of a certain class of magnetic disturbances, usually recorded only at observatories in the daylight zone, on the question of the magnitude and duration of variations in the solar radiation, is discussed. In conclusion, it is indicated how magnetic instruments may effectively supplement other appliances in the detection and measurement of solar radiations of various kinds.

The paper will be published in full in Vol. XX (December 1915 issue) of Terrestrial Magnetism and Atmospheric Electricity.

DEPT. TERRESTRIAL MAGNETISM,
CARNEGIE INSTITUTION, WASHINGTON, D. C.

AN ADAPTATION OF THE KOCH REGISTERING MICROPHOTOMETER TO THE MEASUREMENT OF THE SHARPNESS OF PHOTOGRAPHIC IMAGES.[1]

BY ORIN TUGMAN.

(Communication No. 27 from the Research Laboratory of the Eastman Kodak Company.)

THE Koch registering microphotometer was originally designed to measure the densities of the developed photographic images of spectrum lines, but as the apparatus was used by Koch no attention was given to the resolving power of the apparatus. In many cases inattention to this point will lead to incorrect conclusions drawn from the shape of the registered curve.

The apparatus has been adequately described by Koch in the Annalen der Physik, 39, 1912. The developed negative is passed under an illuminated slit over which is an objective of a microscope which carries a second slit in the focal plane of the objective. The light passing through the microscope falls on a photo-electric cell and generates a current which charges the silvered quartz fiber of a string electrometer. The movement of the quartz fiber is registered on a moving photographic plate. A second photo-electric cell illuminated by the source of lighting the microscope serves as an adjustable leak of the charge on the quartz fiber.

The Koch registering microphotometer was used in the research laboratory of the Eastman Kodak Company to measure the sharpness of photographic images in an investiagtion of resolving power of photographic plates. A carefully ground knife edge was placed on a photographic plate and the whole exposed to a beam of parallel light. The developed negative was passed through the Koch photometer to obtain a curve giving the falling off of density from the edge of the image.

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[1] Abstract of a paper presented at the meeting of the American Physical Society at San Francisco, August 2–7, 1915.

On an ordinary photographic plate the distance at the edge of an image between maximum and minimum density is less than fifty microns and in many cases not over ten microns. It was necessary, therefore, to use a microscope giving sufficient magnification so that the image of the photographic edge would be several times the width of the slit in the focal plane of the microscope objective. It was found that the width of this slit could not be less than .75 mm. when using a four-mm. objective because of the pinhole image formed of the back surface of the objective on the photo-electric cell. If the magnification is less, the width of the slit cannot be less because of the pinhole image formed. With a constant slit width the resolving power of the apparatus is limited by the magnification of the microscope objective.

The registered curve of any density gradient will be in error over a distance (d) at each end represented by $d = s/m$ where (s) is width of slit and (m) is the magnification. If L is the distance over which the density gradient extends the fraction of the curve in error is d/L.

Research Laboratory,
Eastman Kodak Company,
July 20, 1915.

The Resolving Power of Photographic Plates.[1]

By Orin Tugman.

The resolving power of photographic plates has hitherto been investigated by methods which have been suggested by general definitions. The reduced images of fine-lined structures have been photographed and examined under a microscope to determine what lines are resolved. This method is accurate only to the limits of personal judgment and does not reveal the properties which determine the resolving power of an emulsion.

A departure from this method was made by Goldberg[2] who made contact prints through small conical holes in a metal plate. The increase in diameter of the image as the time of exposure was increased was measured and a curve plotted with increase of decimeter against exposure. The slope of this curve was called the turbidity factor and was defined mathematically as $dx/(d(\log I))$ where x is distance from the edge of the image and I is intensity of light measured laterally from the exposed area. The sharpness factor dD/dx is put equal to the photographic factor $dD/(d(\log I))$ divided by $dx/(d(\log I))$, where D is density of the negative. It can be shown that $dx/(d(\log I))$ is not the slope of the curves drawn by Goldberg.

Nutting[3] pointed out that by simple differentiation the density gradient is

$$\frac{dD}{dx} = \frac{dD}{d(\log E)} \frac{d(\log E)}{dx}$$

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[1] Abstract of a paper presented at the meeting of the American Physical Society at San Francisco, August 2–7, 1915.

[2] Goldberg, Photo. Jour., 36, 1912.

[3] Nutting, Photo. Jour., June, 1914.

where E is exposure and that the investigation of resolving power involved a study of the density gradient.

It was argued that inasmuch as the photographic gradient $dD/(d(\log E))$ increases with development and that $(d(\log E))/dx$ is not a function of development the density gradient should increase with development.

A carefully sharpened steel edge was laid on a plate and exposed to a parallel beam of monochromatic light. The density gradient at the edge of the image was measured on the Koch[1] registering microphotometer and also, a Königs-Martens photometer modified for microphotometry. Under ordinary exposures the plates showed no increase of density gradient with development. The density gradient obtained with violet light was greater than with green light in all the cases tried. A process plate dyed yellow gave the greatest density gradient of all plates tried. This may be explained by the increase of optical opacity of the emulsion. The light scattered by the silver halide grains is not affected by the yellow dye but the diffused light is absorbed by the yellow dye and as a result there is very little spreading of the image.

RESEARCH LABORATORY, EASTMAN KODAK CO.,
July 22, 1915.

ON THE ORIGIN AND MAINTENANCE OF THE EARTH'S NEGATIVE CHARGE.[2]

BY W. F. G. SWANN.

The first portion of the paper is devoted to an examination of the possible sources in which an explanation of the observed phenomena of atmospheric electricity may be sought, and to a general discussion of certain broad principles which largely restrict the type of theory available. A brief discussion of former theories is also given in the above light. The second portion of the paper comprises a more detailed consideration of a certain class of hypotheses provisionally formulated for the coördination of atmospheric-electric phenomena. The paper will be published in full in Vols. XX and XXI of Terrestrial Magnetism and Atmospheric Electricity.

DEP'T TERRESTRIAL MAGNETISM,
CARNEGIE INSTITUTION,
WASHINGTON, D. C.

REVIEW OF LABORATORY STUDIES ON THE ZEEMAN EFFECT AT MOUNT WILSON SOLAR OBSERVATORY.[2]

BY HAROLD D. BABCOCK.

A BRIEF account of apparatus and methods used in work on the Zeeman Effect, including descriptions of spectrograph, magnet, means for production of sparks, analyzing devices and other auxiliaries, was followed by illustrations of selected portions of the spectra of iron, vanadium and chromium as affected by a magnetic field. Special attention was directed to the method of standardizing the magnetic fields, which involved the use of a ballistic galvanometer, a number of test coils and a standard mutual inductance in whose primary circuit known currents of electricity could be reversed at will. A small correction was applied to allow for the variation of the field intensity over the volume occupied by the exploring coil, the determination of its amount being made by means of differential measurements with a bismuth spiral. Effects due to variation of field strength over the space occupied by the radiating vapor in the spark were shown for the case of the strong violet lines of chromium, which are very easily reversed.

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[1] Koch—Annalen der Physik, 39, 1913.

[2] Presented at the meeting on Atmospheric Physics of Section B, A. A. A. S., San Francisco, 1915.

Numerous lantern slides were used to illustrate the effects discussed. Typical lines ranging from the class unaffected by a magnetic field to the line of twenty-one components were shown, as well as examples of the use of various analyzers over the slit. Methods of using the echelon and the Fabry-Perot interferometer in the study of weak magnetic fields were also described. In view of the unfinished state of the work, definitive data were not presented.

Mt. Wilson Solar Observatory,
Pasadena, Cal.

Note on the Theory of the Corona.[1]

By W. P. Roop.

THEORIES of the corona have been advanced by Townsend[2] and by Bergen Davis.[3] By strengthening the theoretical basis of one of Townsend's assumptions, and by calling attention to certain features of Davis's treatment, I believe that I can definitely establish the correctness of Townsend's theory.

Townsend's theory is based on the usual empirical equation embodying the results of Baille and Liebig on variation of sparking gradient between parallel plates with distance between the plates. This equation may be given a theoretical basis in the following way.

The current passing between parallel plates is proportional to the expression[4]

$$n = n_0 \frac{(\alpha - \beta)e^{(\alpha-\beta)d}}{\alpha - \beta e^{(\alpha-\beta)d}},$$

where n_0 is the number of ions supplied per second at the negative plate, d is the distance between the plates, and α and β are the numbers of ionizing impacts per centimeter for negative and positive ions respectively. α and β are functions of the gradient X which may be expressed as follows:[4]

$$\alpha = Ne^{-NV/X}$$

and

$$\beta = Me^{-MU/X}.$$

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[1] Abstract of a paper presented at the San Francisco joint meeting of the Physical Society and Section B of the A. A. A. S., August 2–7, 1915.

[2] Townsend, Electrician, June 6, 1913.

[3] Davis, Proc. A. I. E. E., March, 1914.

[4] Townsend, Theory of Ionization by Collision.

Here N and M are the reciprocal free paths, and V and U are the potential falls required to produce ionization, for the negative and positive ions respectively.

If d is held constant, and X gradually increased, a stage is reached at which the denominator of our expression for current becomes zero, and the spark passes. If we now denote by α and β the limiting values at the sparking gradient, we have the relation

$$d = \frac{1}{\alpha} ln \frac{\alpha}{\beta}$$

which becomes, on substitution,

$$d = \frac{e^{NV/X}}{NX}\left(X ln \frac{N}{M} - N V + M U \right),$$

or, approximately,

$$d = \frac{e^{NV/X}}{X}\left(\frac{M}{N} U - V \right).$$

The following table exhibits (1) observed sparking distances for certain values of gradient,[1] (2) the corresponding calculated values, by the empirical formula, and (3) the values calculated by the theoretical formula.

Obs.	Calc. Emp.	Calc. Theoret.
.044	.052	.027
.084	.082	.069
.100	.100	.100
.186	.150	.201
.240	.180	.261
.325	.220	.338
.471	.295	.463
.559	.357	.555
.623	.403	.612
.741	.455	.668
.883	.610	.805
1.067	1.29	1.089
1.144	18.5	1.179

The empirical formula is thus seen to be approximately justified, though the theoretical formula gives closer agreement with observed data.

The calculated results are based on constants determined so as to make the calculated and observed data agree at two points. From the values of the constants thus determined, V, the potential fall required to impart ionizing energy to a negative ion, is calculated to be 7.8 volts. This constitutes an independent determination of this quantity. It is based on the assumption that the negative ion has a mean free path four times as great as the accepted value for a neutral molecule.

The essential difference between the two theories is that according to Davis, ionization by negative ions only occurs, whereas according to Townsend, ionization by positive ions as well is necessary. It is now clear that as far as the discharge between plates is concerned, the discharge sets in when β reaches a certain small value, which nevertheless differs appreciably from zero. It is by the assumption that the conditions about a wire discharging by corona approximate those between plates that Townsend reaches theoretical conclusions agreeing with the observations of Peek and Whitehead.

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[1] Liebig, Phil. Mag., 24, 111, 1887.

The apparent success of Davis's theory seems to be attributable to the fact that the condition arbitrarily assumed to exist when corona appears agrees in form with the condition here deduced. Davis assumes corona to set in when the number of ions produced by a single ion in reaching the wire from a distance attains a certain constant value. In point of fact, it is not this, but the ratio of α to β which must reach a given value. Since Davis's theory is based on the calculation of this constant, the accident by which it does not receive its true meaning happens not to interfere with the success of the calculations in reproducing observed data.

University of California,
Berkeley, Cal.,
August 14, 1915.

The Resistance of a Spark Gap.[1]

By W. P. Boynton.

The behavior of an oscillatory electric circuit is usually discussed on the assumption that the rate of dissipation of energy from the circuit is such as would result from a constant value of the resistance of the circuit, with no losses due to other causes. Many determinations have been made of the equivalent resistances of spark gaps in oscillatory circuits, which have established the fact that these resistances may be and usually are comparatively small. Such values are however not a satisfactory description of such spark resistances, which in all probability have very low initial values, suddenly attained, and then increase rapidly to an infinite value.

As a second approximation to the behavior of such sparks the writer[2] has suggested the assumption that the resistance is constant for a limited period, suddenly becoming infinite. While the number of oscillations to be expected on such an assumption seemed to agree fairly well with the spark photographs available for comparison, this was not satisfying as a description.

The assumption of a constant resistance leads to a graph of the oscillations in which the envelope is the familiar exponential curve, but Zenneck[3] has found experimentally that "when an oscillatory circuit contains a spark gap the decadence of the maxima is approximately represented by a straight line."

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[1] Abstract of a paper presented at the San Francisco joint meeting of the Physical Society and Section B of the A. A. A. S., August 2–7, 1915.

[2] Phys. Rev., 1st Ser., XIX., p. 191, 1904.

[3] Ann. der Physik, 13, p. 822, 1904.

The purpose of this paper is to investigate the values of spark resistance consistent with this observation.

Supposing the circuit to consist of a condenser with its two coatings connected through a metallic inductive circuit and a spark gap, the assumptions that the current may be represented by

$$I = {}_0(l1 - at) \sin bt)$$

and the difference of potential at the terminals of the condenser by

$$V = V_0 \left[(1 - at) \cos bt + \frac{a}{b} \sin bt \right]$$

are consistent with each other, if

$$I_0 = - b C V_0$$

and give satisfactory initial conditions, besides satisfying Zenneck's description, and when substituted in the differential equation

$$V + RI + L dI/dt = 0$$

lead to the results that

$$b = 1/LC \quad \text{and} \quad R/2L = a/(1 - at)$$

and hence that initially, when $t = 0$, $R_0/2L = a$, and hence

$$R = R_0/(1 - at)$$

that is, the resistance of the spark has a finite initial value R_0, and increases regularly, becoming infinite at the time $t = 1/a$, its graph being an equilateral hyperbola, while its conductance decreases uniformly in the same time from its initial value $1/R_0$ to zero. This description of the spark seems plausible, and consistent with our notions of its mechanism, as made up of electrons set free in large numbers at the first passage of the spark, and gradually dissipated, either spontaneously or by whatever means was taken to prevent the persistence of the arc, when that is necessary.

The effective current as shown by a hot-wire ammeter due to a succession of such oscillation trains occurring regularly N times per second would be given by the formula

$$I^2 = NI_0^2/6a = C V_0^2 N/3R,$$

from which the initial resistance is

$$R_0 = N C V_0^2/3I^2,$$

in which all the quantities on the right may be determined experimentally.

One of the interesting applications of this study of spark behavior is to the theory of the optimum conditions for producing long wave trains in a radiotelegraphic transmitting system inductively excited. It is well known that for the practical attainment of this end two adjustments are required, first the tuning of the two circuits to resonance, and second the adjustment of the coupling or mutually inductive effect until a maximum effect is produced in the secondary circuit, as shown usually by a hot-wire ammeter.

It has been shown[1] in the case of two undamped oscillating systems of the same free period with sufficiently weak coupling that there is a surging of energy alternately from one system to the other, such that corresponding states of the two systems may be represented by the forms

$$A_1 \cos mt \cos bt \quad \text{and} \quad A_2 \sin mt \sin bt,$$

in which in our problem $b = \sqrt{1/L_1C_1} = \sqrt{1/L_2C_2}$ and $m = bM/2\sqrt{L_1L_2}$, and $A_2/A_1 = \sqrt{L_2/L_1}$. This may be interpreted of course as two oscillations of the same period but differing in phase by $\pi/2$, and with amplitudes which also vary harmonically with the same phase difference. In the practical case the oscillations are damped, and the primary spark quenched, so that the primary circuit is losing energy both by dissipation and by transfer to the secondary, and its oscillations cease completely when its spark is quenched. The loss by dissipation would correspond to an envelope containing the factor $(1 - at)$ while that due to a transfer to a secondary which was itself radiating and dissipating energy would suggest a factor $e^{-ct} \cos mt$, where m has the same significance as above, and c depends upon the rate of loss of energy in the secondary circuit. It will appear that these two envelopes may be of almost the same shape, and hence we may give the following description of the behavior of the two circuits, which while not exact is yet a closer approximation than is usually given:

$$V_1 = V_{01}(1 - at) \cos bt,$$

$$I_1 = - b C_1 V_{01}(1 - at) \sin bt,$$

$$V_2 = V_{02}e^{-ct} \sin mt \cos bt,$$

$$I_2 = - b C_2 V_{02}e^{-ct} \sin mt \sin bt,$$

in which the terms omitted have contained factors of the order of a/b, c/b, m/b. The optimum effect depends upon such an adjustment of the coupling that $m = \pi a/2$, so that at the time $t = 1/a$ the factor $(1 - at)$ will vanish and $\sin mt$ will become unity. To the first condition corresponds the opening of the primary circuit by the quenching of its spark, so that it no longer receives energy from the secondary, whose further behavior is represented by

$$V_2 = V_{02}e^{-ct} \cos bt,$$

$$I_2 = - b C_2 V_{02}e^{-ct} \sin bt.$$

This system of six equations then very closely represents the decrease of the primary oscillation due to dissipation and transfer of energy, the increase of spark resistance to its infinite value, the increase of the secondary oscillation due to transfer of energy from the primary, and its gradual decay due to dissipation and radiation.

While the curve representing the function $e^{-ct} \cos mt$ when $m = \pi a/2$ lies fairly close to the straight line $1 - at$ for a considerable range of values of c, especial interest seems to attach to the case in which $c/a = (\pi/2)e^{-c/a} = .7454$.

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[1] Rayleigh, Theory of Sound, I., p. 164.

For this value the curve cuts the straight line at $t = 0, 4/9a, 1/a$, and its largest variation is at $t = 7/9a$, the curve giving .191, the line .222, the variation being about 20 per cent. of the odinate, but only 4 per cent. of the largest value.

While for undamped oscillations the ratio of transformation would be $V_{02}/V_{01} = \sqrt{L_2/L_1}$, the maximum secondary E.M.F. would be attained at the time $t = 1/a$ when e^{-ct} becomes $e^{-c/a}$, whose value for $c/a = .7454$ is .4746, hence a probable value would be

$$V_{2max} = .4746\ V_{01}\sqrt{L_2/L_1}$$

or the ratio of transformation would be very nearly one half that for undamped oscillations.

UNIVERSITY OF OREGON,
EUGENE, OREGON,
June 22, 1915.

ELECTROMOTIVE FORCES IN ISOTHERMAL METALLIC CIRCUITS.[1]

BY GILBERT N. LEWIS.

THE accepted statement that electromotive forces can occur in completely metallic circuits only when different parts of the circuit are at different temperatures, is true only when no process involving a diminution in free energy accompanies the transfer of electricity. This is not the case when two amalgams of different concentration are adjacent portions of the electrical circuit. Experiments made in this laboratory by Dr. Adams and Miss Lanman show that a measurable transfer of the dissolved metal accompanies the passage of the current through an amalgam. From such measurements can be calculated the potential of a concentration cell composed of two amalgams of the same metal in contact and connected by platinum wires. The potential thus calculated proves to be an easily measurable quantity, and its experimental determination for a number of amalgams will, it is hoped, afford a means of finding the concentration of electrons in pure mercury.

LABORATORY OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA.

THE SPECTRUM OF THE "TUBE-ARC," AND A COMPARISON WITH LINE-DISSYMMETRIES IN SPARK SPECTRA.[1]

BY ARTHUR S. KING.

THE "tube-arc" is formed when a graphite tube enclosed in a vacuum chamber is burned apart at its middle, with the formation of an arc carrying a large current at low voltage. Substances placed in the tube at the point of rupture are thus vaporized and many peculiarities in their spectra are observed.

The chief features of this source have been previously reported. In a recent study of the spectrum of iron in the tube-arc, special attention was paid to the dissymmetry produced in many of the stronger lines. The density-curves given by the micro-photometer for these lines show their dissymmetry to be equivalent to a displacement of the maximum, usually toward the red. The effect differs greatly in amount for various lines and the grouping on this basis is found to be closely related to the temperature classification of the lines in the furnace spectrum, and less directly to the amounts of their displacement under pressure. The effects resemble closely those observed at the pole of the iron arc, both as to dissymmetry of lines and their relative intensities.

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[1] Abstract of a paper presented at the San Francisco joint meeting of the Physical Society and Section B of the A. A. A. S., August 2–7, 1915.

It was found for iron and other elements that a powerful and disruptive spark produces line dissymmetries which are very similar to those of the tube-arc. The appearance of the characteristic spark lines in the tube-arc is a further resemblance to the spark. As the tube-arc is a low-potential source, the similarity to the spark effect must be looked for in a cause other than high potential gradient. The effects of high electronic speed are being investigated, as this may be a common feature of the two sources.

Mount Wilson Solar Observatory.

A Summary of the Leading Features of Electric Furnace Spectra.[1]

By Arthur S. King.

THE vaporization of metals in the tube resistance-furnace has been found to be a very effective method of studying the spectrum under conditions which differ in many respects from those prevailing in the flame, arc, or spark. The temperature of the vapor in the carbon tube may be controlled through a wide range, and the resulting changes in the spectrum have been observed for a number of elements. It is found that, beginning with a few lines at low temperature, the richness of the spectrum may be gradually increased until the number of lines is comparable with that given by the arc, but many differences in relative intensity of lines are found between the furnace and arc spectra.

The features given special study in the spectra at various furnace temperatures are the successive appearance of groups of lines as the temperature rises, and the varying rates of increase in the intensity of lines belonging to different groups. The classification arrived at in this way is found to be closely connected with the behavior of these groups of lines under other physical conditions.

In addition to the variation of spectra with temperature, the furnace has been found well adapted to the study of absorption effects, pressure displacements of either emission or absorption lines, the effect of various atmospheres, banded spectra, and the spectra of mixed vapors.

Mount Wilson Solar Observatory.

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[1] Abstract of a paper presented at the San Francisco joint meeting of the Physical Society and Section B of the A. A. A. S., August 2–7, 1915.

THE THUNDERSTORM.

BY W. J. HUMPHREYS.[1]

ACCORDING to Simpson's well-supported theory, the electric separation that gives rise to lightning is produced by the disruption of raindrops in the air and the transfer of the resulting negative spray to higher altitudes by convection currents. From this theory it follows, in full accord with observation, that thunderstorms must be confined almost exclusively to large cumulus clouds, and therefore occur most frequently when the surface temperature and the absolute humidity both are high.

Such peculiar phenomena of the thunderstorm as the gentle breeze toward it, the more or less violent wind gusts immediately in front of and away from it, the abrupt drop in temperature, the equally abrupt rise in pressure, the occurrence of hail and the various forms and movements of the accompanying clouds may all be explained as consequences of a rising current starting in front of the storm and becoming especially vigorous within the cumuli, together with a corresponding down rush of totally different air from within and below the lower cloud levels. The temperature contrast essential to this peculiar circulation is maintained by the simultaneous action of a heat source, condensation, and a heat sink, evaporation; the former occurring within the cloud; the latter all the way between the cloud and the surface.

Lightning, in its various forms, though merely incidental to and in no sense the cause of the wind and rain of a thunderstorm, often is the most impressive of all its phenomena. When analyzed by a rotating camera its vivid sinuous streaks are either single, as they appear to the eye; multiple, consisting of several single streaks occurring along identical paths but at unequal intervals; or complex, producing a picture analogous to that of a waving, plaid ribbon. Occasionally a streak of lightning persists during an appreciable length of time and then gradually fades away, thus producing through its end-on and therefore brighter portions, the phenomenon known as beaded or pearl lightning.

Sheet lightning, as seen in distant clouds, appears to be only the diffused and reflected light of ordinary streak lightning. Rocket, or slow moving, lightning and ball lightning have too often been reported by good observers to permit of their classification with things wholly subjective, however baffling at present may be the difficulty of explaining them.

It is often stated that the lightning discharge consists of many high frequency oscillations. There is much evidence, however, in favor of the idea that the discharge is either unidirectional or else very heavily damped. The question is still an open one, as are many others in connection with the thunderstorm, and should tempt further and conclusive investigation.

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[1] Abstract of a paper presented at the joint meeting of the Physical Society and Section B of the A. A. A. S., in Berkeley, August 3, 1915.

NEW BOOKS.

Prinzipien der Atomdynamik. III Teil. By J. Stark. Leipzig: S. Hirzel, 1915. Pp. xvi+280. Price, 9 Mk.

This volume, which has to do with "Die Elektrizität in Chemischen Atom" and is illustrated with ninety-four diagrams constitutes an attempt on the part of the author to explain a number of the properties of matter from a physical, chemical, and crystallographical standpoint by means of certain assumptions regarding the manner in which valency or surface electrons are bound to atoms and to the role these play in molecular groupings of atoms. Among the subjects treated are the arrangement and energy of the valency electrons in the benzol ring, electrolytic dissociation in solutions, catalysis, conduction of electricity in metals, the relation of band spectra to the chemical constitution of molecules, optical dispersion, molecular and atomic refraction, and the rotation of the plane of polarization of light by different substances. The assumptions made by the author in regard to the character and functions of the electronic bonds are remarkably simple, and with these he has succeeded in linking up a mass of scattered and hitherto disjointed information regarding a great number of very diverse phenomena. J. C. McL.

Physical Laboratory Manual. Chaffee. Cambridge: Harvard University Press, 1914. Pp. vi + 128.

Harvard led the way among American Universities in making a sharp distinction between beginning, or first-year physics, offered in that institution for pupils who do not present physics for entrance, and the second-year course assigned for those who have had the beginning course. The present manual contains the directions for the 34 laboratory experiments in this second-year course. It is apparently the successor to Professor Sabine's manual and represents a distinct advance in the choice of material for such a course and in the elimination of material which is on the whole better adapted to the beginning course. It is on this choice that the chief merits and demerits of college manuals lie. The judgment shown in Professor Chaffee's manual is especially commendable. R. A. M.

X-Rays and Crystal Structure. W. H. Bragg and W. L. Bragg. London: G. Bell and Sons, Ltd., 1915. Pp. vii + 228.

Of the numerous investigators who have applied Laue's brilliant discovery to the investigation of X-rays and of crystalline structure, none have been so successful in disentangling the many complications of the subject and in advancing rapidly and surely toward a completer knowledge as the two Braggs, father and son. It is well known that their work was greatly facilitated by the fortunate "reflection" point of view due to W. L. Bragg. It is very interesting to observe that this is mathematically identical with the theory first given by Laue; the only change is a transformation of axes such that, along two of the axes, the interference of the ray considered shall be of zero order. But, as not infrequently happens, this apparently trivial change makes all the difference between fertility and rapid progress on the one hand, and confusion and delay on the other.

No one who reads the present book, however, will remain under the delusion that the success of the authors in their investigations is due entirely to a fortunate point of view; on the contrary, one is constantly moved to admiration by the acuteness and insight which they display and the directness with which they proceed to their goal, both in experimental methods and in the interpretation of their results.

After a brief introductory chapter, a simple theory of the diffraction of the rays by the crystal atoms is given and the construction and use of the X-ray spectrometer is described. A brief summary of the properties of X-rays—especially the work of Barkla—is contained in Chapter IV. The following chapter is devoted to an elementary but very clear exposition of crystal structure and of the notation used by mineralogists; although it deals only with very simple forms, this chapter will doubtless be useful to many physicists whose knowledge of crystallography, like that of the present reviewer, is rudimentary. Chapter VI deals with X-ray spectra and the interesting relations which have been found to subsist among the characteristic radiations of different elements. The next four chapters take up in detail the question of the analysis of crystal structure; the ingenuity and resourcefulness shown in these pages is very remarkable. In Chapter XI the authors discuss the intensity of X-ray reflection and its dependence on various factors. The book closes with an analysis of some of Laue's photographs from the "reflection" point of view. H. A. B.

An Introduction to Laboratory Physics. LUCIUS TUTTLE, Associate in Physics, Jefferson Medical College. Philadelphia: Jefferson Laboratory of Physics. Pp. xi + 150.

A series of fifteen excellent exercises on the scientific treatment of data in physical measurements, a very handy and useful little book for every student of laboratory physics beginning or advanced. R. A. M.

Annuaire Pour L'An 1915, Publie Par Le Bureau Des Longitudes. Avec une Notice scientifique. Paris: Gauthier-Villars, 1915.

The main portion of the volume, namely 754 pages, consists of the usual astronomical tables, weights and measures, interest and actuaries tables. Appended thereto is a treatise of 173 pages entitled "Les méthodes d'examen des miroirs et des objectifs" by M. G. Bigourdan, which merits examination by those in this field of work. F. B.

Vocational Mathematics. By WM. H. DOOLEY. Boston: D. C. Heath and Co., 1915. Pp. viii+341.

This book has been prepared to meet the criticism that a pupil graduates from the usual course in mathematics without being able to "commercialize" or apply his knowledge in such a way as to be able to meet the needs of trade and industry. F. B.

Theory of Measurement—A Manual for Physics Students. By JAMES S. STEVENS, Professor of Physics, University of Maine. Pp. vi + 80. D. Van Nostrand Co. $1.25.

A very practical little laboratory book on the Theory of Probability in its relation to the treatment of errors in physical measurements. Not so well adapted to beginners as Tuttle's book but excellent for those having some knowledge of the calculus. R. A. M.

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ERRATA.

Vol. V., May, 1915, article by S. A. Moss, entitled "Integration of Thermodynamic Equations for an Imperfect Gas"; the last term in equation 25, page 444, should be divided by $f^{-1}(p)$ so as to read $+ Tv_p / f^{-1}(p)$.

Vol. VI., October, 1915, article by H. O. Taylor, entitled "A Mechanical Process for Constructing Harmonic Analysis Schedules for Waves Having Even and Odd Harmonics":

p. 304, equation (3), second term of right-hand member, should read, $C_2 \sin (2\omega t + \alpha_2)$;
p. 305, schedule for A_9, v_6 should be $+$;
p. 305, value of $y_{3n/2}$, last term should read, $+ B_n$;
p. 308, line 19, should read, at the beginning *of counting*;
p. 309, mark for second footnote should be 2.

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